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(54) Titre : COMPOSES SILANES UTILISES COMME ADDITIFS DANS LES ELECTROLYTES DE CELLULES ELECTROCHIMIQUES
(54) Title: SILANE COMPOUNDS AS ADDITIVES IN ELECTROLYTES FOR ELECTROCHEMICAL CELLS

(57) Abrégé/Abstract:
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Silane compounds as additives in electrolytes for electrochemical cells

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Lithium ion batteries are among the most promising systems for mobile applications. Fields of use range from high-value electronic equipment (e.g. mobile telephones, camcorders) to batteries for electrically driven motor vehicles.

These batteries consist of cathode, anode, separator and a nonaqueous electrolyte. As cathode, use is typically made of Li(MnMe₃)₂O₄, Li(CoMe₄)O₂, Li(CoNiₓMe₃)O₂ or other lithium intercalations and insertion compounds. Anodes can consist of lithium metal, carbon, graphite, graphitic carbon or other lithium intercalation and insertion compounds or alloys. Electrolytes used are solutions of lithium salts such as LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂ or LiC(CF₃SO₂)₃ and mixtures thereof in aprotic solvents.

Owing to the sensitivity to water and other protic contaminants of the electrolyte salt LiPF₆ frequently used in lithium ion batteries, these electrolytes always have a measurable content of hydrofluoric acid. In addition to this, the electrolyte has an HF content of at least 50 ppm resulting from its method of manufacture. In addition, HF can be formed by heating of the system. The hydrofluoric acid formed reacts readily with the various components of the battery.

Graphite electrodes are usually coated with alkyl carbonates, lithium carbonates, lithium hydroxides and lithium oxides. The hydrofluoric acid reacts with this coating. In electrolytes comprising LiPF₆ as
electrolyte salt, it has been able to be shown that the impedance of the battery increases continually. This is attributable to attack on the carbonate coating and the formation of an LiF film.

5 HF reacts with the coating according to the following equations:
\[ \text{Li}_2\text{CO}_3 + 2\text{HF} \rightarrow 2\text{LiF} + \text{H}_2\text{CO}_3 \]
\[ \text{LiOH} + \text{HF} \rightarrow \text{LiF} + \text{H}_2\text{O} \]
\[ \text{Li}_2\text{O} + 2\text{HF} \rightarrow 2\text{LiF} + \text{H}_2\text{O}. \]

In contrast to the original coating, the LiF-containing film has very poor, if any, permeability to Li ions.

10 The prior art discloses the addition of additives which are intended to react with HF and thus prevent the formation of the LiF film.

Many additives for use in lithium ion batteries have been mentioned in the literature. Thus, for example, tributylamine is used as an HF trap. This additive reduces the HF content very effectively, but it is not stable to electrochemical oxidation. It is irreversibly decomposed above about 3.5 V relative to Li/Li⁺.

15 In JP 08321311, various acetates and oxalates and also silanes are employed as additives. These form a layer on the anode which is said to prevent the reactions between electrolyte and anode.

20 In contrast to the prior art, the present invention does not seek to remove HF from the electrolyte or to form a new film. Instead, the new starting point aims to dissolve lithium fluoride which has been formed and thus stabilize the impedance of the battery.

25 It is therefore an object of the present invention to provide additives which counter film formation on the
electrodes and have a sufficiently high electrochemical stability.

The object of the invention is achieved by the use of compounds of the following formula:

\[ \text{SiR}^1\text{R}^2\text{R}^3\text{R}^4 \]

where

\[ \text{R}^1-\text{R}^4 \] are each H, \n\n\[ \text{C}_y\text{F}_{2y+1-z}\text{H}_z, \]
\[ \text{OC}_y\text{F}_{2y+1-z}\text{H}_z, \]
\[ \text{OC}(\text{O})\text{C}_y\text{F}_{2y+1-z}\text{H}_z, \]
\[ \text{OSO}_2\text{C}_y\text{F}_{2y+1-z}\text{H}_z \]

with \( 1 \leq x < 6, 1 \leq y \leq 8 \) and \( 0 \leq z \leq 2y+1 \) and \( \text{R}^1-\text{R}^4 \) are identical or different and are each

an aromatic ring selected from the group consisting of phenyl and naphthyl which may be unsubstituted or monosubstituted or polysubstituted by F, \( \text{C}_y\text{F}_{2y+1-z}\text{H}_z \) or \( \text{OC}_y\text{F}_{2y+1-z}\text{H}_z, \text{OC}(\text{O})\text{C}_y\text{F}_{2y+1-z}\text{H}_z, \text{OSO}_2\text{C}_y\text{F}_{2y+1-z}\text{H}_z, \text{N}(\text{C}_n\text{F}_{2n+1-z}\text{H}_z)_2 \) or

a heterocyclic aromatic ring selected from the group consisting of pyridyl, pyrazyl and pyrimidyl which may each be monosubstituted or polysubstituted by F, \( \text{C}_y\text{F}_{2y+1-z}\text{H}_z \) or \( \text{OC}_y\text{F}_{2y+1-z}\text{H}_z, \text{OC}(\text{O})\text{C}_y\text{F}_{2y+1-z}\text{H}_z, \text{OSO}_2\text{C}_y\text{F}_{2y+1-z}\text{H}_z, \text{N}(\text{C}_n\text{F}_{2n+1-z}\text{H}_z)_2 \), as additive. The silane compounds are used as additives in electrolytes consisting of a lithium-containing inorganic electrolyte salt or lithium-containing organic electrolyte salt dissolved in aprotic solvents.

The silane compounds are dissolved in electrolytes which are customarily used in electrochemical cells, preferably in nonaqueous secondary lithium batteries.
It has been found that tetracoordinated silane compounds, in particular tetramethoxysilane, ethyl-triacetoxysilane, diphenylmethoxysilane, difluorodiphenylsilane and triethylsilyl fluoromethanesulfonate, are suitable additives for electrochemical cells.

It has surprisingly been found that silane compounds can dissolve LiF to high concentrations in organic aprotic solvents. The additives used according to the invention can prevent the formation of an LiF film on the electrodes. This enables the impedance of the battery to be stabilized.

The additives have good electrochemical stability. It has been found that the oxidation stability of the silane compounds is sufficiently high for use in electrochemical cells, preferably in lithium ion batteries.

The silane compounds can be used in electrolytes comprising conventional electrolyte salts. Suitable electrolyte salts are, for example, ones selected from the group consisting of LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂, LiN(CF₃CF₂SO₂)₂ or LiC(CF₃SO₂)₃ and mixtures thereof.

The electrolytes may further comprise organic isocyanates (DE 199 44 603) to reduce the water content.

It is also possible for compounds of the formula

$$\left[\left[ \left( R^1 \right) \left( R^2 \right) \left( R^3 \right) \right] A \right] K t \left[ \text{N} \left( \text{CF}_3 \right) \right]_2$$

where

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

R¹, R² and R³ are identical or different and are each

H, halogen, substituted and/or unsubstituted alkyl CₙH₂ₙ₊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 CₘH₂ₘ₋₁, monosubstituted or polysubstituted and/or unsubstituted phenyl, substituted and/or unsubstituted heteroaryl,

where

A may be included in various positions in R¹, R² and/or R³,

Kₜ can be included in a cyclic or heterocyclic ring,

the groups bound to Kₜ may be identical or different,

and

n  is 1-18
m  is 3-7
k  is 0, 1-6
l  is 1 or 2 when x=1 and is 1 when x=0
x  is 0, 1
y  is 1-4,

to be present (DE 9941566). The process for preparing the compounds comprises reacting an alkali metal salt of the formula

D⁺·N(CF₃)₂
where $D^*$ is selected from the group of alkali metals, in a polar organic solvent with a salt of the formula

$$\left[ \left\{ \left[ R^1 (CR^2 R^3)_k \right] Ax \right\}_y Kt \right]^+ \cdot E$$

where

$Kt$, $A$, $R^1$, $R^2$, $R^3$, $k$, $l$, $x$ and $y$ are as defined above and

$E$ is $F^-$, $Cl^-$, $Br^-$, $I^-$, $BF_4^-$, $ClO_4^-$, $AsF_6^-$, $SbF_6^-$ or $PF_6^-$. The compounds used according to the invention can also be present in electrolytes comprising compounds of the formula

$$X^- (\text{CYZ})_m \cdot SO_2 N (CR^1 R^2 R^3)_2$$

where

$X$ is $H$, $F$, $Cl$, $CnF_{2n+1}$, $CnF_{2n-1}$, $(SO_2)_k N (CR^1 R^2 R^3)_2$

$Y$ is $H$, $F$, $Cl$

$Z$ is $H$, $F$, $Cl$

$R^1$, $R^2$, $R^3$ are each $H$ and/or alkyl, fluoroalkyl, cycloalkyl

$m$ is 0-9 and when $X=H$, $m=0$

$n$ is 1-9

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

prepared by reacting partially fluorinated or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents (DE 199 466 73).

It is also possible to use electrolytes comprising complex salts of the formula (DE 199 51 804)

$$M^{x+} \left[ \text{E} \right]_{x/y}^-$$

where:
x, y are each 1, 2, 3, 4, 5, 6

$M^{x+}$ is a metal ion

E is a Lewis acid selected from the group consisting of $BR^1R^2R^3$, $AlR^2R^3$, $PR^2R^4R^5$, $AsR^2R^4R^5$, $VR^2R^4R^5$,
R$^1$ to R$^5$ are identical or different, may be joined
directly to one another by a single or double bond and
are in each case individually or together

a halogen (F, Cl, Br),

an alkyl or alkoxy radical (C$_1$ to C$_6$) which may be
partially or fully substituted by F, Cl, Br,

an aromatic ring selected from the group consisting of
phenyl, naphthyl, anthracenyl and phenanthrenyl which
may be bound via oxygen and may be unsubstituted or
monosubstituted to hexasubstituted by alkyl (C$_1$ to C$_6$)
or F, Cl, Br,

an aromatic heterocyclic ring selected from the group
consisting of pyridyl, pyrazyl and pyrimidyl which may
be bound via oxygen and may be unsubstituted or
monosubstituted to tetrasubstituted by alkyl (C$_1$ to C$_6$)
or F, Cl, Br, and

Z is OR$_6$, NR$_6R^7$, CR$_6R^7R^8$, OSO$_2$R$_6$, N(SO$_2$R$_6$)(SO$_2$R$^7$),
C(SO$_2$R$_6$)(SO$_2$R$^7$)(SO$_2$R$^8$), OCOR$_6$, where

R$^6$ to R$^8$ are identical or different, may be joined
directly to one another by a single or double bond and
are in each case individually or together

a hydrogen atom or as defined for R$^2$ to R$^5$,

prepared by reacting an appropriate boron or phosphorus
Lewis acid-solvent adduct with a lithium or
tetraalkylammonium imide, methanide or triflate.
It is also possible for borate salts (DE 199 59 722) of the formula

\[
\begin{array}{c}
\text{M}^{x+} \\
\text{B} \\
\text{R}^1 \quad \text{R}^2 \\
\text{R}^3 \quad \text{R}^4 \\
\end{array}
\]

\[\text{y}^{-}\]

where:

M is a metal ion or tetraalkylammonium ion \(x, y\) are each 1, 2, 3, 4, 5 or 6
\(\text{R}^1\) to \(\text{R}^4\) are identical or different alkoxy or carboxy radicals (C\(_1\)-C\(_4\)) which may be joined directly to one another by 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 boric ester in an aprotic solvent with a suitable hydroxyl or carboxyl compound in a ratio of 2:1 or 4:1.

The compounds used according to the invention can also be employed in electrolytes comprising lithium fluoroalkylphosphates of the formula

\[
\text{Li}^+[\text{PF}_x(\text{C}_y\text{F}_{2y+1-z}\text{H}_z)_6-x]^{-}
\]

where

\(1 \leq x \leq 5\)
\(3 \leq y \leq 8\)
\(0 \leq z \leq 2y + 1\)

and the ligands (C\(_y\)F\(_{2y+1-z}\)H\(_z\)) may be identical or different, with the exception of compounds of the formula

\[
\text{Li}^+[\text{PF}_a(\text{CH}_b\text{F}_c(\text{CF}_3)_d)_e]^{-}
\]
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, with the provisos that b and c are not at the same time 0 and the sum of a + e is 6 and the ligands \( \text{CH}_6\text{F}_e(\text{CF}_3)_d \) may be identical or different (DE 100 089 55). The process for preparing lithium fluoroalkylphosphates comprises fluorinating at least one compound of the formula

\[
H_m\text{P}(C_n\text{H}_{2n+1})_{3-m}, \\
\text{OP}(C_n\text{H}_{2n+1})_3, \\
\text{Cl}_m\text{P}(C_n\text{H}_{2n+1})_{3-m}, \\
F_m\text{P}(C_n\text{H}_{2n+1})_{3-m}, \\
\text{Cl}_o\text{P}(C_n\text{H}_{2n+1})_{5-o}, \\
F_o\text{P}(C_n\text{H}_{2n+1})_{5-o},
\]

where in each case

\( 0 < m < 2, 3 < n < 8 \) and \( 0 < o < 4 \), by electrolysis in hydrogen fluoride, fractionating the resulting mixture of fluorination products by extraction, phase separation and/or distillation, and reacting the resulting fluorinated alkylphosphorane in an aprotic solvent or solvent mixture with lithium fluoride in the absence of moisture, and purifying and isolating the resulting salt by customary methods.

The compounds used according to the invention can also be employed in electrolytes comprising salts of the formula

\[
\text{Li}[\text{P}(\text{OR}^1)_a(\text{OR}^2)_b(\text{OR}^3)_c(\text{OR}^4)_d\text{F}_e]
\]

where \( 0 < a+b+c+d \leq 5 \) and \( a+b+c+d+e = 6 \), and \( R^1 \) to \( R^4 \) are, independently of one another, alkyl, aryl or heteroaryl radicals, where at least two of the radicals \( R^1 \) to \( R^4 \) may be joined directly to one another by a single or
double bond (DE 100 16 801). The compounds are prepared by reacting phosphorus(V) compounds of the formula

\[ P(\text{OR}_1)^a(\text{OR}_2)^b(\text{OR}_3)^c(\text{OR}_4)^d \text{F}_e \]

where \(0 < a+b+c+d \leq 5\) 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.

It is also possible for ionic liquids of the formula

\[ K^+A^- \]

where:

- \(K^+\) is a cation selected from the group consisting of

where \(R^1\) to \(R^5\) are identical or different, may be joined directly to one another by a single or double bond and are in each case individually or together:
- H,
- halogen,
- an alkyl radical (C₁ to C₈) which may be partially or fully substituted by further groups, preferably F, Cl, N(CₙF(₂n+1-ₓ)Hₓ)₂, O(CₙF(₂n+1-ₓ)Hₓ), SO₂(CₙF(₂n+1-ₓ)Hₓ), CₙF(₂n+1-ₓ)Hₓ where 1<ₓ<6 and 0<ₓ<13

and
A⁻ is an anion of the formula

[B(OR¹)ₙ(OR²)ₘ(OR³)ₚ(OR⁴)ₚ⁻]

where 0≤n, m, o, p≤4 and m+n+o+p=4

where R¹ to R⁴ are different or identical in pairs, may be joined directly to one another by a single or double bond and are in each case individually or together

an aromatic ring selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl which may be unsubstituted or monosubstituted or polysubstituted by CₙF(₂n+1-ₓ)Hₓ where 1<ₓ<6 and 0<ₓ<13 or halogen (F, Cl, Br),

an aromatic heterocyclic ring selected from the group consisting of pyridyl, pyrazyl and pyrimidyl which may be unsubstituted or monosubstituted or polysubstituted by CₙF(₂n+1-ₓ)Hₓ where 1<ₓ<6 and 0<ₓ<13 or halogen (F, Cl, Br),

an alkyl radical (C₁ to C₈) which may be partially or fully substituted by further groups, preferably F, Cl, N(CₙF(₂n+1-ₓ)Hₓ)₂, O(CₙF(₂n+1-ₓ)Hₓ), SO₂(CₙF(₂n+1-ₓ)Hₓ), CₙF(₂n+1-ₓ)Hₓ where 1<ₓ<6 and 0<ₓ<13,

or OR¹ to OR⁴ are
individually or together an aromatic or aliphatic carboxyl, dicarboxyl, oxysulfonyl or oxycarboxyl radical which may be partially or fully substituted by further groups, preferably F, Cl, N(CₙFₙ₋ₓHₓ)₂, O(CₙF(2n+1-x)Hₓ), SO₃(CₙF(2n+1-x)Hₓ), CₙF(2n+1-x)Hₓ where 1<n<6 and 0<x≤13 (DE 100 265 65), to be present in the electrolyte.

Ionic liquids K⁺A⁻ where K⁺ is as defined above and

A⁻ is an ion of the formula

\[ \text{PF}_x(C_yF_{2y+1-2H_z})_{6-x} \]

where

1 ≤ x < 6
1 ≤ y ≤ 8 and
0 ≤ z ≤ 2y+1

may also be present (DE 100 279 95).

The compounds used according to the invention can also be present in electrolytes comprising compounds of the following formula:

\[ \text{NR}^1\text{R}^2\text{R}^3 \]

where

R¹ and R² are each H, CₙF₂y+1-zH₂, or (CₙF₂n-mHₘ)m, X, where X is an aromatic or heterocyclic radical, and

R³ is (CₙF₂n-mHₘ)Y, where Y is a heterocyclic radical, or
(CₙF₂n-mHₘ)p, Z, where Z is an aromatic radical,

and n, m, o, p, y and z fulfil the following conditions:

0 ≤ n ≤ 6,
0 ≤ m ≤ 2n,
\[
2 \leq o \leq 6, \\
0 \leq p \leq 2o, \\
1 \leq y \leq 8 \text{ and} \\
0 \leq z \leq 2y+1,
\]
to reduce the acid content in aprotic electrolyte systems in electrochemical cells.

It is also possible for fluoroalkylphosphates of the formula

\[
M^{n+}[PF_x(C_yF_{2y+1-z}H_z)_{6-x}]_n^{-}
\]

where

\[
1 \leq x \leq 6 \\
1 \leq y \leq 8 \\
0 \leq z \leq 2y+1 \\
1 \leq n \leq 3 \text{ and}
\]

\(M^{n+}\) is a monovalent to trivalent cation, in particular:

\[
NR^1R^2R^3R^4, \\
PR^1R^2R^3R^4, \\
P(NR^1R^2)_{k}R^3R^4_{m}R^4_{k-m} \text{ (where } k=1-4, m=0-3 \text{ and } k+m\leq4),
\]

\[
C(NR^1R^2)(NR^3R^4)(NR^5R^6), \\
C(aryl)_3, \text{ Rb or tropylium,}
\]

where \(R^1\) to \(R^8\) are each \(H\), alkyl and aryl (\(C_1-C_9\)) which may be partially substituted by \(F\), \(Cl\) or \(Br\),

with the exception of \(M^{n+} = Li^+, Na^+, Cs^+, K^+\) and \(Ag^+\), to be present. These fluoroalkylphosphates are obtainable by reacting phosphoranes with a fluoride or metal fluoroalkylphosphates with a fluoride or chloride in organic aprotic solvents (DE 100 388 58).

The electrolyte can also comprise a mixture comprising

a) at least one lithium fluoroalkylphosphate salt of the formula
Li$^\text{+}[\text{PF}_x(C_y\text{F}_{2y+1-z}\text{H}_z)_6-x]^-$

where

\[1 \leq x \leq 5\]
\[1 \leq y \leq 8\] and
\[0 \leq z \leq 2y + 1\]

and the ligands \((C_y\text{F}_{2y+1-z}\text{H}_z)\) are in each case identical or different and

b) at least one polymer (DE 100 58 264).

Tetrakisfluoroalkylborate salts of the formula

\[
M^{\text{m}+}[\text{BR}_4]^{-}\rangle^n
\]

where

\(M^{\text{m}+}\) is a monovalent, divalent or trivalent cation,

the ligands \(R\) are in each case identical and are each \((C_y\text{F}_{2x+1})\) where \(1 \leq x \leq 8\)

and \(n = 1, 2, 3\) (DE 100 558 11), can also be present in the electrolyte. The process for preparing tetrakisfluoroalkylborate salts comprises fluorinating at least one compound of the formula \(M^{\text{m}+}[\text{B(CN)}_4]^{-}\rangle^n\) where \(M^{\text{m}+}\) and \(n\) are as defined above, by reaction with at least one fluorinating agent in at least one solvent and purifying and isolating the resulting fluorinated compound by customary methods.

The electrolyte can also comprise borate salts of the formula

\[
M^{\text{m}+}[\text{BF}_x(C_y\text{F}_{2y+1-z}\text{H}_z)_4-x]^{-}\rangle^n
\]

where:
1 < x < 3, 1 ≤ y ≤ 8 and 0 ≤ z ≤ 2y + 1 and

M is a monovalent to trivalent cation (1 ≤ n ≤ 3),
with the exception of potassium and barium,

in particular:
Li,
NR₂R³R⁴, PR₅R⁶R⁷R⁸, P(NR₅R₆)ₖR₇ₘR₉ₖ₋ₘ (where k = 1-4, m = 0-3
and k+m≤4) or
C(NR₅R₆)(NR₇R₈)(NR₉R₊), where
R₁ to R₄ are each C₇F₂₇₋₁₋ₙHₙ and
R₅ to R₊ are each H or C₇F₂₇₋₁₋ₙHₙ or

an aromatic heterocyclic cation, in particular a
nitrogen- and/or oxygen- and/or sulfur-containing
aromatic heterocyclic cation (DE 101 031 89). The
process for preparing these compounds comprises

a) reacting BF₃-solvent complexes 1:1 with alkyllithium
while cooling, slowly warming the mixture and then
removing most of the solvent and subsequently filtering
off the solid and washing it with a suitable solvent, or

b) reacting lithium salts in a suitable solvent 1:1
with B(CF₃)F₃⁻ salts, stirring the mixture at elevated
temperature and, after removing the solvent, admixing
the reaction mixture with aprotic nonaqueous solvents,
preferably solvents which are used in electrochemical
cells, and drying, or

b) reacting B(CF₃)F₃⁻ salts 1:1 to 1:1.5 with lithium
salts in water at elevated temperature and heating the
mixture at the boiling point for from 0.5 to 2 hours,
removing the water and admixing the reaction mixture
with aprotic nonaqueous solvents, preferably solvents
which are used in electrochemical cells, and drying.
The electrolyte can also comprise fluoroalkylphosphate salts of the formula

\[ \text{M}^{m+} \left( [\text{PF}_x(\text{C}_y\text{F}_{2y+1-z}\text{H}_z)_5-x]^- \right)_n \]

where

\( \text{M}^{m+} \) is a monovalent, divalent or trivalent cation,
1 \( \leq x \leq 5, \)
1 \( \leq y \leq 8 \) and

0 \( \leq z \leq 2y + 1, \) \( n = 1, 2 \) or 3 and the ligands \((\text{C}_y\text{F}_{2y+1-z}\text{H}_z)\) are in each case identical or different, with the exception of the fluoroalkylphosphate salts in which \( \text{M}^{m+} \) is a lithium cation and the salts

\[ \text{M}^+(\text{PF}_4(\text{CF}_3)_2)^- \] where \( \text{M}^+ = \text{Cs}^+, \text{Ag}^+ \) or \( \text{K}^+ \),

\[ \text{M}^+(\text{PF}_4(\text{C}_2\text{F}_5)_2)^- \] where \( \text{M}^+ = \text{Cs}^+ \),

\[ \text{M}^+(\text{PF}_3(\text{C}_2\text{F}_5)_3)^- \] where \( \text{M}^+ = \text{Cs}^+, \text{K}^+, \text{Na}^+ \) or para-\( \text{Cl}(\text{C}_6\text{H}_4)\text{N}_2^+ \),

\[ \text{M}^+(\text{PF}_3(\text{C}_6\text{F}_7)_3)^- \] where \( \text{M}^+ = \text{Cs}^+, \text{K}^+, \text{Na}^+ \), para-\( \text{Cl}(\text{C}_6\text{H}_4)\text{N}_2^+ \) or para-\( \text{O}_2\text{N}(\text{C}_6\text{H}_4)\text{N}_2^+ \) (DE 100 558 12). The process for preparing these fluoroalkylphosphate salts comprises fluorinating at least one compound of the formula

\[ \text{H}_x\text{P}(\text{C}_s\text{H}_{2s+1})_{3-r}, \]
\[ \text{OP}(\text{C}_s\text{H}_{2s+1})_{3-r}, \]
\[ \text{Cl}_r\text{P}(\text{C}_s\text{H}_{2s+1})_{3-r}, \]
\[ \text{F}_r\text{P}(\text{C}_s\text{H}_{2s+1})_{3-r}, \]
\[ \text{Cl}_r\text{P}(\text{C}_s\text{H}_{2s+1})_{5-t} \text{ and/or} \]
\[ \text{F}_r\text{P}(\text{C}_s\text{H}_{2s+1})_{5-t}, \]

where in each case

0 \( \leq r \leq 2 \)
3 \( \leq s \leq 8 \) and
0 \( \leq t \leq 4 \),

by electrolysis in hydrogen fluoride, fractionating the resulting mixture of fluorination products and reacting the resulting fluorinated alkylphosphorane in an aprotic solvent or solvent mixture with a compound of
the formula $M^{n+}(F^{-})_n$ where $M^{n+}$ and $n$ are as defined
above, in the absence of moisture and purifying and
isolating the resulting fluoroalkylphosphate salt by
 customary methods.

5

The compounds used according to the invention can also
be employed in electrolytes for electrochemical cells
which comprise anode material consisting of 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 producing this anode
material comprises

a) preparing a suspension or a sol of the metal or
alloy core in urotropin,

b) emulsifying the suspension with $C_5$-$C_{12}$-hydrocarbons,

c) precipitating the emulsion onto the metal or alloy
cores and

d) converting the metal hydroxides or oxyhydroxides
into the corresponding oxide by heating the system.

25

The compounds used according to the invention can also
be employed in electrolytes for electrochemical cells
having cathodes comprising customary lithium
intercalation and insertion compounds or else
electrochemical cells having cathode materials which
consist of lithium mixed oxide particles coated with
one or more metal oxides (DE 199 22 522). They can also
consist of lithium mixed oxide particles which are
coated with one or more polymers (DE 199 46 066) and
are obtained by a process in which the particles are
suspended in a solvent and the coated particles are
subsequently filtered off, dried and if appropriate
calcined. The compounds used according to the invention
can likewise be employed in systems having cathodes
which consist of lithium mixed oxide particles which

are coated with one or more layers of alkali metal compounds and metal oxides (DE 100 14 884). The process for producing these materials comprises suspending the particles in an organic solvent, adding an alkali metal salt compound suspended in an organic solvent, adding metal oxides dissolved in an organic solvent, admixing the suspension with a hydrolysis solution and subsequently filtering off, drying and calcining the coated particles. The compounds used according to the invention can likewise be employed in systems which comprise anode materials comprising doped tin oxide (DE 100 257 61). This anode material is produced by:

a) admixing a tin chloride solution with urea,

b) admixing the solution with urotropin and a suitable doping compound,

c) emulsifying the resulting sol in petroleum ether,

d) washing the gel obtained and removing the solvent by filtration with suction and

e) drying and heat-treating the gel.

The compounds used according to the invention can likewise be employed in systems which comprise anode materials comprising reduced tin oxide (DE 100 257 62). This anode material is produced by

a) admixing a tin chloride solution with urea,

b) admixing the solution with urotropin,

c) emulsifying the resulting sol in petroleum ether,

d) washing the gel obtained and removing the solvent by filtration with suction,

e) drying and heat-treating the gel and
f) treating the SnO₂ obtained with a reducing gas stream in an oven through which gas can be passed.

5 The invention accordingly provides an electrolyte for nonaqueous electrochemical cells, preferably for secondary lithium batteries, whose performance is improved, e.g. the formation of an LiF film is minimized with corresponding reduction of the impedance, by addition of specific additives.

The invention will now be illustrated by a general example.

15 Examination of the solubility of lithium fluoride

From 0.01 to 10% by weight of LiF, based on the electrolyte, are added to a solvent mixture selected from the group consisting of EC, DMC, PC, DEC, EC, PC, BC, VC, cyclopentanones, sulfolanes, DMS, 3-methyl-1,3-oxazolidin-2-one, DMC, DEC, γ-butyrolactone, EMC, MPC, BMC, EPC, BEC, DPC, 1,2-diethoxymethane, THF, 2-methyltetrahydrofuran, 1,3-dioxolane, methyl acetate, ethyl acetate and mixtures thereof. The suspension is stirred at room temperature.

For comparison, the same solution is, in parallel, admixed with from 0.01 to 10% by weight, preferably from 0.1 to 5% by weight, of silanes of the formula (I)

\[ \text{SiR}^1\text{R}^2\text{R}^3\text{R}^4 \quad (I) \]

where

\[ \text{R}^1-\text{R}^4 \quad \text{are each H,} \]
\[ \text{CyF}_{2y+1-z}\text{H}_z, \]
\[ \text{OCyF}_{2y+1-z}\text{H}_z, \]
\[ \text{OC(O)CyF}_{2y+1-z}\text{H}_z, \]
\[ \text{OSO}_2\text{CyF}_{2y+1-z}\text{H}_z, \]
where \(1 \leq x \leq 6\), \(1 \leq y \leq 8\) and \(0 \leq z \leq 2y + 1\) and
\(R^1 - R^4\) are identical or different and are each

5 an aromatic ring selected from the group consisting of
phenyl and naphthyl which may be unsubstiututed or
monosubstituted or polysubstituted by \(F, C\_{yF_{2y+1}} - H_z\) or
\(OC\_{yF_{2y+1}} - H_z\), \(OC(O)C\_{yF_{2y+1}} - H_z\), \(OSO_2C\_{yF_{2y+1}} - H_z\), \(N(C\_{nF_{2n+1}} - H_z)_2\), or

10 a heterocyclic aromatic ring selected from the group
consisting of pyridyl, pyrazyl and pyrimidyl which may
each be monosubstituted or polysubstituted by \(F,
C\_{yF_{2y+1}} - H_z\) or \(OC\_{yF_{2y+1}} - H_z\), \(OC(O)C\_{yF_{2y+1}} - H_z\), \(OSO_2C\_{yF_{2y+1}} - H_z\),
\(N(C\_{nF_{2n+1}} - H_z)_2\). Particular preference is given to using
silane compounds selected from the group consisting of
tetramethoxysilane, ethyltriacetoxyisilane, diphenylmethoxysilane, difluorodiphenylsilane and
triethylsilyl fluoromethanesulfonate. The suspension is

20 stirred at room temperature.

The silanes dissolve lithium fluoride to differing
degrees.

25 The following examples illustrate the invention without
restricting it.

**Examples**

30 **Example 1**

**Solubility of LiF in EC with and without Si additive**

0.5 or 1.0 mol/l of LiF are added to 500 ml of EC/DMC

35 (1:1). The suspensions are stirred at room temperature
for 24 hours. In both cases, no dissolution of LiF is
observed.
To determine the influence of silane compounds, the experiments are repeated with the addition of in each case equimolar amounts of the silane. Table 1 shows the results obtained.

<table>
<thead>
<tr>
<th>Silane compound</th>
<th>0.5 mol/l of LiF</th>
<th>1.0 mol/l of LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethoxysilane</td>
<td>+</td>
<td>o</td>
</tr>
<tr>
<td>Ethyltriacetoxyisilane</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Diphenylmethoxysilane</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Difluorodiphenylsilane</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Triethylsilyl fluoromethanesulfonate</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Table 1

do: slight sediment 
+: no sediment 
++: no sediment, LiF is quickly dissolved

Ethyltriacetoxyisilane, diphenylmethoxysilane, difluorodiphenylsilane and triethylsilyl fluoromethanesulfonate are able to dissolve LiF, with difluorodiphenylsilane and triethylsilyl fluoromethanesulfonate being particularly effective.

Example 2

Oxidation stability of the silanes

In a measurement cell having a platinum working electrode, a lithium counterelectrode and a lithium reference electrode, 5 cyclovoltammograms are recorded in succession in each case. Here, the potential is firstly increased from the rest potential at a rate of 10 mV/s to 6.0 V relative to Li/Li⁺ and subsequently brought back to the rest potential.

The electrolyte used is a 1 molar solution of LiPF₆ in EC/DMC which in each case contains 5% of silane additive. Table 2 shows the results obtained. Figure 1
shows the cyclovoltammogram obtained using ethyltriacetoxyisilane as additive.

<table>
<thead>
<tr>
<th>Silane compound</th>
<th>$E_{\text{ox}}$ relative to Li/Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethoxysilane</td>
<td>4.4 V</td>
</tr>
<tr>
<td>Ethyltriacetoxyisilane</td>
<td>5.3 V</td>
</tr>
<tr>
<td>diphenylmethoxysilane</td>
<td>4.8 V</td>
</tr>
<tr>
<td>Difluorodiphenylsilane</td>
<td>5.5 V</td>
</tr>
<tr>
<td>Triethylsilyl</td>
<td>5.2 V</td>
</tr>
<tr>
<td>fluoromethanesulfonate</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

All silanes have sufficient stability for use in electrochemical cells.

Example 3

Cyclability of graphite and LiMn$_2$O$_4$ in silane-containing electrolytes

Cycling experiments were carried out at room temperature and at 60°C under galvanostatic conditions in half cells having a lithium counterelectrode and a graphite or LiMn$_2$O$_4$ working electrode.

For this purpose, 1% of the respective silane additive was added to an electrolyte consisting of 1 mol/l of LiPF$_6$ in EC:DEC:DMC (2:1:2).

Figures 2-7 show the results of the cycling tests obtained at 60°C, with Figures 2 and 3 showing the results for the additive-free electrolyte as reference.

The cyclability of the electrodes both in respect of the cycle yield and the cycling stability can be improved by addition of silanes.
Claims

1. Electrolyte consisting of a lithium-containing inorganic electrolyte salt or lithium-containing organic electrolyte salt dissolved in aprotic solvents, characterized in that it comprises at least one silane compound as additive.

2. Electrolyte according to Claim 1, characterized in that the additives are selected from the group consisting of tetracoordinated silane compounds.

3. Electrolyte according to Claim 1 or 2, characterized in that the additives are silane compounds of the formula

\[ \text{SiR}_1^3 \text{R}_2^4 \text{R}_3^4 \text{R}_4^4 \quad (1) \]

where

\[ \text{R}_1^3 - \text{R}_4^4 \] are each \( H, \)
\( C_{yF2y+1-z}H_2, \)
\( OC_{yF2y+1-z}H_2, \)
\( OC(O)C_{yF2y+1-z}H_2, \)
\( OSO_2C_{yF2y+1-z}H_2 \)

and \( 1 \leq x \leq 6 \)
\( 1 \leq y \leq 8 \) and \( 0 \leq z \leq 2y+1 \)

and \( \text{R}_1^3 - \text{R}_4^4 \) are identical or different and are each an aromatic ring selected from the group consisting of phenyl and naphthyl which may be unsubstituted or monosubstituted or polysubstituted by \( F, \) \( C_{yF2y+1-z}H_2 \) or \( OC_{yF2y+1-z}H_2, \)
\( OC(O)C_{yF2y+1-z}H_2, \) \( OSO_2C_{yF2y+1-z}H_2, \) \( N(C_{nF2n+1-z}H_2)_2 \) or

a heterocyclic aromatic ring selected from the group consisting of pyridyl, pyrazyl and pyrimidyl which may each be monosubstituted or
polysubstituted by F, C\textsubscript{y}F\textsubscript{2y+1-z}H\textsubscript{z} or OC\textsubscript{y}F\textsubscript{2y+1-z}H\textsubscript{z}, OC(O)C\textsubscript{y}F\textsubscript{2y+1-z}H\textsubscript{z}, OSO\textsubscript{2}C\textsubscript{y}F\textsubscript{2y+1-z}H\textsubscript{z}, N(C\textsubscript{n}F\textsubscript{2n+1-z}H\textsubscript{z})\textsubscript{2}.

4. Electrolyte according to any of Claims 1 to 3, characterized in that the additives are selected from the group consisting of tetramethoxysilane, ethyltriacetoxy silane, diphenylmethoxysilane, difluorodiphenylsilane and triethylsilyl-fluoromethanesulfonate.

5. Electrolyte according to any of Claims 1 to 4, characterized in that the additives are present in the electrolyte in concentrations of from 0.01 to 10% by weight.

6. Electrolyte according to any of Claims 1 to 5, characterized in that the additives are present in the electrolyte in concentrations of from 0.1 to 5% by weight.

7. Electrochemical cell consisting of cathode, anode, separator and electrolyte, characterized in that it comprises an electrolyte according to any of Claims 1 to 6.

8. Use of silane compounds as additive in electrochemical cells, batteries and secondary lithium batteries.

9. Use of silane compounds of the formula

\[ \text{SiR}^1\text{R}^2\text{R}^3\text{R}^4 \]  \hspace{1cm} (I)

where R\textsubscript{1}, R\textsubscript{2}, R\textsubscript{3} and R\textsubscript{4} are as defined above, as additive in electrochemical cells, batteries and secondary lithium batteries.

10. Use of silane compounds according to Claim 8 or 9 for dissolving lithium fluoride.
11. Use of silane compounds according to Claim 8 or 9 in combination with other lithium salts.

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Figure 2: 1 mol/l of LiPF$_6$ in EC:DEC:DMC = 2:1:2, graphite electrode, 60°C (reference I)

![Graph](image1)

Figure 3: 1 mol/l of LiPF$_6$ in EC:DEC:DMC = 2:1:2, LiMn$_2$O$_4$ electrode, 60°C (reference II)

![Graph](image2)
Figure 4: 1 mol/l of LiPF₆ in EC:DEC:DMC = 2:1:2 +1% of tetramethoxysilane, graphite electrode, 60°C

Figure 5: 1 mol/l of LiPF₆ in EC:DEC:DMC = 2:1:2 +1% of tetramethoxysilane, LiMn₂O₄ electrode, 60°C
Figure 6: 1 mol/l of LiPF₆ in EC:DEC:DMC = 2:1:2 +1% of ethyltriacetoxyisilane, graphite electrode, 60°C

Figure 7: 1 mol/l of LiPF₆ in EC:DEC:DMC = 2:1:2 +1% of ethyltriacetoxyisilane, LiMn₂O₄ electrode, 60°C