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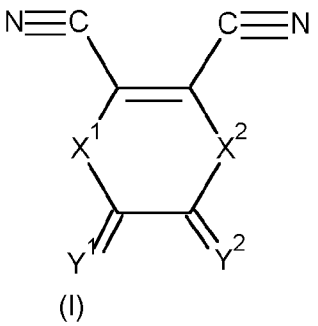
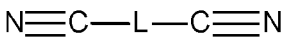
(54) Title: ELECTROCHEMICAL CELLS USING COMBINATIONS OF NITRILE COMPOUNDS AS ADDITIVES



(I)



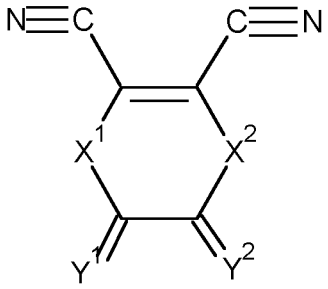
(II)

(57) Abstract: An electrolyte composition containing at least one cyclic dinitrile compound of formula (I) wherein X^1 and X^2 are independently from each other selected from $N(R^1)$, $P(R^1)$, O, and S, and Y^1 and Y^2 are independently from each other selected from (O), (S), (PR^2) and (NR^2); and at least one linear dinitrile compound of formula (II) wherein L is a $-(CH_2)_n-$ chain which may be interrupted by O, S, or NR5, or may contain a double or a triple bond or may be substituted.

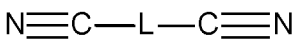
Electrochemical cells using combinations of nitrile compounds as additives

Description

The present invention relates to an electrolyte composition containing at least one cyclic dinitrile compound of formula (I)



and at least one linear dinitrile compound of formula (II)



wherein X^1, X^2, Y^1, Y^2, and L are defined as described below and to an electrochemical cell comprising said electrolyte composition.

Storing electrical energy is a subject of still growing interest. Efficient storage of electric energy would allow electric energy to be generated when it is advantageous and used when needed. Secondary electrochemical cells are well suited for this purpose due to their reversible conversion of chemical energy into electrical energy and vice versa (rechargeability). Secondary lithium batteries are of special interest for energy storage since they provide high energy density and specific energy due to the small atomic weight of the lithium ion, and the high cell voltages that can be obtained (typically 3 to 4.9 V) in comparison with other battery systems. For that reason, these systems have become widely used as a power source for many portable electronics such as cellular phones, laptop computers, mini-cameras, etc.

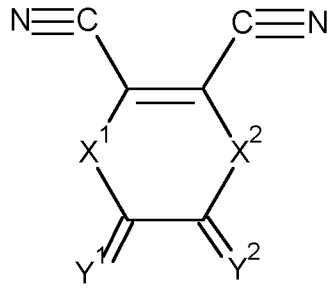
Secondary lithium batteries like lithium ion batteries typically comprise electrolyte compositions containing one or more organic aprotic solvents liked non-aqueous solvents like organic carbonates, ethers, esters and ionic liquids, at least one conducting salt like $LiPF_6$ and optionally one or more additives for enhancing the performance of electrolyte composition and battery. Useful additives are for example SEI additives, flame retardant additives, water scavenger, overcharge protection additives. A lot of research is ongoing in respect to additives for use in electrolyte compositions to further improve the performance of the electrochemical cell containing the electrolyte composition in many different aspects, e.g. cycle life time, high temperature characteristics, safety, etc.

WO 2015/007554 A1 discloses the use of cyclic dinitriles as additives in electrolyte compositions to obtain lithium secondary ion batteries showing improved capacity retention.

Other aspects of the performance of an electrochemical cell are the internal resistance, increase of internal resistance over the lifetime of the battery and gas evolution over the life of the battery. There is the need for additives for electrolyte compositions showing less internal resistance, less internal resistance increase and less gas evolution than common electrolyte compositions. It is in particular desirable if these additives do not have a detrimental effect on other properties of the electrochemical cells in which they are used.

It was an object of the present invention to provide an electrolyte composition yielding secondary batteries with improved properties like lower resistance increase and lower or similar gas evolution. A further object of the present invention was to provide secondary batteries of high energy density and/or higher operating voltage having good performance characteristics like lower impedance build up and lower resistance.

This object is achieved by an electrolyte composition containing at least one compound of formula (I)



(I)

wherein

X^1 and X^2 are independently from each other selected from $N(R^1)$, $P(R^1)$, O, and S;

R^1 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_{10} alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^3, $C(O)R^3$, $C(NR^3)R^4$, and $C(O)OR^3$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3a}$, $OS(O)_2R^{3a}$, $S(O)_2R^{3a}$, OR^{3a}, $C(O)R^{3a}$, $C(O)OR^{3a}$, $NR^{3a}R^{3b}$, and $NC(O)R^{3a}R^{3b}$;

Y^1 and Y^2 are independently from each other selected from (O), (S), (PR^2) and (NR^2),

R^2 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, (hetero)C_3-C_6 cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^{2a} and $C(O)R^{2a}$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{2b}$, $OS(O)_2R^{2b}$, $S(O)_2R^{2b}$, OR^{2b}, $C(O)R^{2b}$, $C(O)OR^{10b}$, $NR^{2b}R^{2c}$, and $NC(O)R^{2b}R^{2c}$; and

R^{2a}, R^{2b} and R^{2c} are independently from each other selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl, (hetero)cycloalkyl,

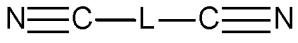
alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN,

R^3, R^4, R^{3a}, and R^{3b} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, and C_6-C_{13} (hetero)aralkyl, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3c}$, $OS(O)_2R^{3c}$, $S(O)_2R^{3c}$, OR^{3c}, $C(O)R^{3c}$, $C(O)OR^{3c}$, $NR^{3c}R^{3d}$, and $NC(O)R^{3c}R^{3d}$; and

R^{3c} and R^{3d} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl, (hetero)cycloalkyl, alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN;

and

at least one compound of formula (II)



(II)

wherein

L is a $-(CH_2)_n-$ chain wherein one or more CH_2 groups of the $-(CH_2)_n-$ chain which are not directly bound to a CN group may be replaced by O, S or $N(R^5)$ and wherein a C-C single bond between two adjacent CH_2 groups of the $-(CH_2)_n-$chain may be replaced by a C-C double bond or a C-C triple bond and wherein one or more H of the $-(CH_2)_n-$chain may be substituted independently from each other by F and/or optionally fluorinated C_1-C_{10} alkyl and wherein two H of a (CH_2) group of the $-(CH_2)_n-$chain may be substituted by $=C(R^6R^7)$;

n is an integer from 1 to 12;

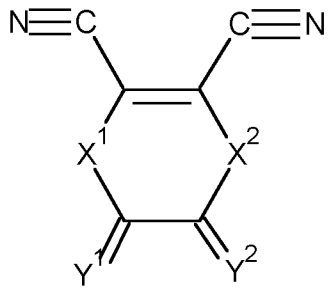
R^5, R^6 and R^7 are independently from each other selected from H and optionally fluorinated C_1-C_6 alkyl.

The problem is further solved by an electrochemical cell comprising the electrolyte composition as described above.

The addition of at least one compound of general formula (I) and at least one compound of formula (II) to an electrolyte composition for rechargeable electrochemical cells leads to less resistance increase and less resistivity of the electrochemical cells.

In the following the invention is described in detail.

The inventive electrolyte composition contains at least one cyclic dinitrile of formula (I)



(I)

wherein

X^1 and X^2 are independently from each other selected from $N(R^1)$, $P(R^1)$, O, and S, preferably X^1 and X^2 are independently from each $N(R^1)$ and O, more preferred X^1 and X^2 are $N(R^1)$;

R^1 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_{10} alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^3, $C(O)R^3$, $C(NR^3)R^4$, and $C(O)OR^3$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3a}$, $OS(O)_2R^{3a}$, $S(O)_2R^{3a}$, OR^{3a}, $C(O)R^{3a}$, $C(O)OR^{3a}$, $NR^{3a}R^{3b}$, and $NC(O)R^{3a}R^{3b}$, preferably R^1 is independently from each other selected from H, C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_2-C_6 alkynyl, wherein alkyl, alkenyl, and alkynyl may be substituted by one or more substituents selected from F, CN, $OS(O)_2R^{3a}$, $S(O)_2R^{3a}$, OR^{3a}, $C(O)R^{3a}$, and $C(O)OR^{3a}$;

Y^1 and Y^2 are independently from each other selected from (O), (S), (PR^2) and (NR^2), preferably Y^1 and Y^2 are (O);

R^2 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^{2a} and $C(O)R^{2a}$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{2b}$, $OS(O)_2R^{2b}$, $S(O)_2R^{2b}$, OR^{2b}, $C(O)R^{2b}$, $C(O)OR^{10b}$, $NR^{2b}R^{2c}$, and $NC(O)R^{2b}R^{2c}$; preferably R^2 is selected from H, C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_2-C_6 alkynyl, wherein alkyl, alkenyl, and alkynyl may be substituted by one or more substituents selected from F, CN, $OS(O)_2R^{2a}$, $S(O)_2R^{2a}$, OR^{2a}, $C(O)R^{2a}$, and $C(O)OR^{2a}$;

R^{2a}, R^{2b} and R^{2c} are independently from each other selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl, (hetero)cycloalkyl, alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN, preferably R^{2a}, R^{2b} and R^{2c} are independently from each other selected from H, C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_2-C_6 alkynyl, wherein alkyl, alkenyl, and alkynyl may be substituted by one or more substituents selected from F and CN;

R^3, R^4, R^{3a}, and R^{3b} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, and C_6-C_{13} (hetero)aralkyl, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one

or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3c}$, $OS(O)_2R^{3c}$, $S(O)_2R^{3c}$, OR^{3c}, $C(O)R^{3c}$, $C(O)OR^{3c}$, $NR^{3c}R^{3d}$, and $NC(O)R^{3c}R^{3d}$; and

R^{3c} and R^{3d} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl, (hetero)cycloalkyl, alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN;

The term "C_1-C_{10} alkyl" as used herein means a straight or branched saturated hydrocarbon group with 1 to 10 carbon atoms having one free valence, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, iso-pentyl, 2,2-dimethylpropyl, n-hexyl, iso-hexyl, 2-ethyl hexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, n-decyl and the like. Preferred are f C_1-C_6 alkyl, more preferred are C_1-C_4 alkyl groups and most preferred are methyl, ethyl, and n- and iso-propyl.

The term "C_3 to C_6 (hetero)cycloalkyl" as used herein means a saturated 3- to 6-membered hydrocarbon cycle having one free valence wherein one or more of the C- atoms of the saturated cycle may be replaced independently from each other by a heteroatom selected from N, S, O and P. Examples of C_3-C_6 cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, preferred is cyclohexyl. Examples of C_3-C_6 hetero cycloalkyl are oxiranyl, tetrahydrofuryl, pyrrolidyl, piperidyl and morpholinyl.

The term "C_2-C_{10} alkenyl" as used herein refers to an unsaturated straight or branched hydrocarbon group with 2 to 10 carbon atoms having one free valence. Unsaturated means that the alkenyl group contains at least one C-C double bond. C_2-C_{12} alkenyl includes for example ethenyl, 1-propenyl, 2-propenyl, 1-n-butenyl, 2-n-butenyl, iso-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl and the like. Preferred are C_2-C_8 alkenyl groups, more preferred are C_2-C_6 alkenyl groups, even more preferred are C_2-C_4 alkenyl groups and in particular ethenyl and propenyl, the preferred propenyl is 1-propen-3-yl, also called allyl.

The term "C_3-C_6 (hetero)cycloalkenyl" as used herein refers to a cyclic unsaturated hydrocarbon group with 3 to 6 carbon atoms having one free valence wherein one or more C-atoms may be replaced by N, O or S. Unsaturated means that the cycloalkenyl contains at least one C-C double bond. Examples of C_3-C_6 (hetero)cycloalkenyl are cyclopropen, cycolbuten, cyclopenten, and cyclohexen.

The term "C_2 to C_{10} alkynyl" as used herein refers to an unsaturated straight or branched hydrocarbon group with 2 to 10 carbon atoms having one free valence, wherein the hydrocarbon group contains at least one C-C triple bond. C_2-C_{10} alkynyl includes for example ethynyl, 1-propynyl, 2-propynyl, 1-n-butinyl, 2-n-butynyl, iso-butinyl, 1-pentynyl, 1-hexynyl, -heptynyl, 1-octynyl, 1-nonynyl, 1-decynyl and the like. Preferred are C_2-C_{10} alkynyl, more

preferred are C_2-C_6 alkynyl, even more preferred are C_2-C_4 alkynyl, in particular preferred are ethynyl and 1-propyn-3-yl (propargyl).

The term "C_5 to C_7 (hetero)aryl" as used herein denotes an aromatic 5- to 7-membered hydrocarbon cycle or condensed cycles having one free valence wherein one or more of the C-atoms of the aromatic cycle(s) may be replaced independently from each other by a heteroatom selected from N, S, O and P. Examples of C_5-C_7 (hetero)aryl are pyrrolyl, furanyl, thiophenyl, pyridinyl, pyranyl, thiopyranyl, and phenyl. Preferred is phenyl.

The term "C_6-C_{13} (hetero)aralkyl" as used herein denotes an aromatic 5- to 7-membered hydrocarbon cycle substituted by one or more C_1-C_6 alkyl wherein one or more of the C- atoms of the aromatic cycle may be replaced independently from each other by a heteroatom selected from N, S, O and P. The C_6-C_{13} (hetero)aralkyl group contains in total 6 to 13 C- and heteroatomsand has one free valence. The free valence may be located in the aromatic cycle or in a C_1-C_6 alkyl group, i.e. C_6-C_{13} (hetero)aralkyl group may be bound via the (hetero)aromatic part or via the alkyl part of the group. Examples of C_6-C_{13} (hetero)aralkyl are methylphenyl, 2-methylpyridyl, 1,2-dimethylphenyl, 1,3-dimethylphenyl, 1,4-dimethylphenyl, ethylphenyl, 2-propylphenyl, benzyl, CH_2-pyridyl, and the like.

Preferred compounds of formula (I) are selected from compounds of formula (I) wherein Y^1 and Y^2 are (O).

Also preferred are compounds of formula (I) wherein both X^1 and X^2 are same or different and selected independently from (O) and N(R^1), more preferred X^1 and X^2 are independently from each other selected from N(R^1) and even more preferred X^1 and X^2 are same and selected from N(R^1). Within this embodiment it is preferred that Y^1 and Y^2 are (O). This includes e.g. compounds of formula (I) wherein

X^1 and X^2 are independently from each other N(R^1); and

Y^1 and Y^2 are (O).

More preferred are compounds of formula (I) wherein

X^1 and X^2 are independently from each other N(R^1);

each R^1 is independently from each other selected from H, C_1-C_6 alkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, and C_6-C_{13} (hetero)aralkyl, wherein alkyl, alkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, $OS(O)_2R^{3a}$, $S(O)_2R^{3a}$, OR^{3a}, $C(O)R^{3a}$, and $C(O)OR^{3a}$;

R^{3a} is selected from C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_2-C_6 alkynyl, wherein alkyl, alkenyl, and alkynyl may be substituted by one or more substituents selected from F, CN, and OR^{3c};

R^{3c} is selected from H, and C_1-C_6 alkyl which may be substituted by one or more substituents selected from F and CN; and

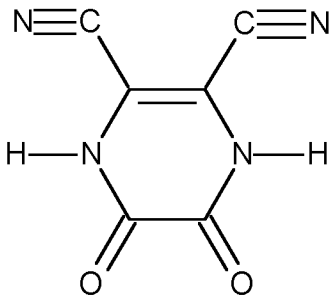
Y^1 and Y^2 are (O).

Even more preferred are compounds of formula (I) wherein

X^1 and X^2 are independently from each other $N(R^1)$;
each R^1 is independently from each other selected from H, C_1-C_6 alkyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, and C_6-C_{13} (hetero)aralkyl, wherein alkyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F and CN; and
Y^1 and Y^2 are (O).

Most preferred are compounds of formula (I) wherein
X^1 and X^2 are independently from each other $N(R^1)$;
each R^1 is independently from each other selected from H, C_1-C_6 alkyl, C_2-C_6 alkynyl, and C_5-C_7 (hetero)aryl, wherein alkyl, alkynyl and (hetero)aryl may be substituted by one or more substituents selected from F and CN; and
Y^1 and Y^2 are (O).

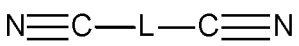
A particularly preferred example of compounds of formula (I) is compound (I.1):



(I.1)

Compounds of formula (I) and their preparation are described in detail in WO 2015/007554 A1. Compound of formula (I.1) is commercially available.

The inventive electrolyte composition additionally contains at least one compound of formula (II)



(II)

wherein
L is a $–(CH_2)_n–$ chain wherein one or more CH_2 groups of the $–(CH_2)_n–$ chain which are not directly bound to a CN group may be replaced by O, S or $N(R^5)$ and wherein a C-C single bond between two adjacent CH_2 groups of the $–(CH_2)_n–$chain may be replaced by a C-C double bond or a C-C triple bond and wherein one or more H of the $–(CH_2)_n–$chain may be substituted independently from each other by F, NR^6R^6, SR^6, OR^6, and/or optionally fluorinated C_1-C_{10} alkyl and wherein two H of a (CH_2) group of the $–(CH_2)_n–$chain may be substituted by $=C(R^6R^7)$;
n is an integer from 1 to 12;
R^5, R^6 and R^7 are independently from each other selected from H and optionally fluorinated C_1-C_6 alkyl.

n is an integer from 1 to 12, preferably from 1 to 10, more preferred an integer from 2 to 8, and even more preferred an integer from 4 to 8.

Preferred compounds of formula (II) are compounds wherein
L is a $–(CH_2)_n–$ chain wherein one or more CH_2 groups of the $–(CH_2)_n–$ chain which are not directly bound to a CN group may be replaced by O or S and wherein a C-C single bond between two adjacent CH_2 groups of the $–(CH_2)_n–$chain may be replaced by a C-C double bond or a C-C triple bond and wherein one or more H of the $–(CH_2)_n–$chain may be substituted independently from each other by F, NR^6R^6, SR^6, OR^6, and optionally fluorinated C_1-C_4 alkyl and wherein two H of a (CH_2) group of the $–(CH_2)_n–$chain may be substituted by $=C(R^6R^7)$ with R^6 and R^7 are selected independently from H and optionally fluorinated C_1-C_4 alkyl; and
n is an integer from 1 to 10, preferred from 2 to 8.

More preferred compounds of formula (II) are compounds wherein L is a $–(CH_2)_n–$ chain and n is an integer from 1 to 10, preferred from 2 to 8, more preferred from n is an integer from 2 to 7, e.g. succinonitrile, glutaronitrile, adiponitrile, pimelonitrile, suberonitrile, and azelanitrile.

Examples of compounds of formula (II) are adipodinitrile, succinodinitrile, trans-3-hexenedinitrile, 2- hexenedinitrile, dodecanedinitrile, suberonitrile, pimelonitrile, subeconitrile, azelanitrile, glutaronitrile, 2-methlyeneglutaronitrile, 2-methylglutaronitrile, 2-methyladiponitrile, 2-methylsuccinonitrile, 2-methylsuberonitrile, 2-methylazelanitrile, 2,2-dimethylglutaronitrile, 2,2-dimethyladiponitrile, 2,2-dimethylsuberonitrile, 2,2-dimethylazelanitrile, 2,2-dimethylsuccinonitrile, 2,2,4,4-tetramethylglutaronitrile, 2,2,4,4-tetramethylsuccinonitrile, 2,2,4,4-tetramethyladiponitrile, 2,2,4,4-tetramethylsuberonitrile, 2,2,4,4-tetramethylazelanitrile, 3-[2-(2-cyanoethoxy)ethoxy]propanenitrile, 3-(2-cyanoethoxy)propanenitrile, and 3,3'-thiodipropiodinitrile, preferred are adipodinitrile and succinodinitrile.

The minimum total concentration of compounds of formula (I) and formula (II) in the electrolyte composition is 0.005 wt.-%, usually the total concentration of compounds of formula (I) and formula (II) in the electrolyte composition is in the range of 0.005 to 10 wt.-% of the total amount of the electrolyte composition, preferably the total concentration of compounds of formula (I) and formula (II) in the electrolyte composition is in the range of 0.01 to 6 wt.-% and most preferred in the range of 0.05 to 5 wt.-%, based on the total amount of the electrolyte composition. The term "wt.-%" as used herein means percent by weight.

The molar ratio of compound(s) of formula (I) and compound(s) of formula (II), i.e. the molar ratio of the entire amount of compounds of formula (I) and the entire amount of compounds of formula (II) present in the electrolyte composition is in the range of from 1 : 99 to 99 : 1, preferably in the range of from 1 : 50 to 50 : 1 and most preferred in the range of from 1 : 20 to 20 : 1.

The electrolyte composition preferably contains at least one aprotic organic solvent, more preferred at least two aprotic organic solvents. According to one embodiment the electrolyte composition may contain up to ten aprotic organic solvents.

The at least one aprotic organic solvent is preferably selected from cyclic and acyclic organic carbonates, di-C_1-C_{10}-alkylethers, di-C_1-C_4-alkyl-C_2-C_6-alkylene ethers and polyethers, cyclic ethers, cyclic and acyclic acetales and ketales, orthocarboxylic acids esters, cyclic and acyclic esters of carboxylic acids, cyclic and acyclic sulfones, and cyclic and acyclic nitriles and dinitriles.

More preferred the at least one aprotic organic solvent is selected from cyclic and acyclic carbonates, di-C_1-C_{10}-alkylethers, di-C_1-C_4-alkyl-C_2-C_6-alkylene ethers and polyethers, cyclic and acyclic acetales and ketales, and cyclic and acyclic esters of carboxylic acids, even more preferred the electrolyte composition contains at least one aprotic organic solvent selected from cyclic and acyclic carbonates, and most preferred the electrolyte composition contains at least two aprotic organic solvents selected from cyclic and acyclic carbonates, in particular preferred the electrolyte composition contains at least one aprotic solvent selected from cyclic carbonates and at least one aprotic organic solvent selected from acyclic carbonates.
The aprotic organic solvents may be partly halogenated, e.g. they may be partly fluorinated, partly chlorinated or partly brominated, and preferably they may be partly fluorinated. “Partly halogenated” means, that one or more H of the respective molecule is substituted by a halogen atom, e.g. by F, Cl or Br. Preference is given to the substitution by F. The at least one solvent may be selected from partly halogenated and non-halogenated aprotic organic solvents i.e. the electrolyte composition may contain a mixture of partly halogenated and non-halogenated aprotic organic solvents.

Examples of cyclic carbonates are ethylene carbonate (EC), propylene carbonate (PC) and butylene carbonate (BC), wherein one or more H of the alkylene chain may be substituted by F and/or an C_1 to C_4 alkyl group, e.g. 4-methyl ethylene carbonate, monofluoroethylene carbonate (FEC), and cis- and trans-difluoroethylene carbonate. Preferred cyclic carbonates are ethylene carbonate, monofluoroethylene carbonate and propylene carbonate, in particular ethylene carbonate.

Examples of acyclic carbonates are di-C_1-C_{10}-alkylcarbonates, wherein each alkyl group is selected independently from each other, preferred are di-C_1-C_4-alkylcarbonates. Examples are e.g. diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and methylpropyl carbonate. Preferred acyclic carbonates are diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC).

In one embodiment of the invention the electrolyte composition contains mixtures of acyclic oganic carbonates and cyclic organic carbonates at a ratio by weight of from 1:10 to 10:1, preferred of from 5:1 to 1:5.

According to the invention each alkyl group of the di-C_1-C_{10}-alkylethers is selected independently from the other. Examples of di-C_1-C_{10}-alkylethers are dimethylether, ethylmethylether, diethylether, methylpropylether, diisopropylether, and di-n-butylether.

Examples of di-C_1-C_4-alkyl-C_2-C_6-alkylene ethers are 1,2-dimethoxyethane, 1,2-diethoxyethane, diglyme (diethylene glycol dimethyl ether), triglyme (triethyleneglycol dimethyl ether), tetraglyme (tetraethyleneglycol dimethyl ether), and diethylenglycoldiethylether.

Examples of suitable polyethers are polyalkylene glycols, preferably poly-C_1-C_4-alkylene glycols and especially polyethylene glycols. Polyethylene glycols may comprise up to 20 mol% of one or more C_1-C_4-alkylene glycols in copolymerized form. Polyalkylene glycols are preferably dimethyl- or diethyl- end-capped polyalkylene glycols. The molecular weight M_w of suitable polyalkylene glycols and especially of suitable polyethylene glycols may be at least 400 g/mol. The molecular weight M_w of suitable polyalkylene glycols and especially of suitable polyethylene glycols may be up to 5 000 000 g/mol, preferably up to 2 000 000 g/mol.

Examples of cyclic ethers are 1,4-dioxane, tetrahydrofuran, and their derivatives like 2-methyl tetrahydrofuran.

Examples of acyclic acetals are 1,1-dimethoxymethane and 1,1-diethoxymethane. Examples of cyclic acetals are 1,3-dioxane, 1,3-dioxolane, and their derivatives such as methyl dioxolane.

Examples of acyclic orthocarboxylic acid esters are tri-C_1-C_4 alkoxy methane, in particular trimethoxymethane and triethoxymethane. Examples of suitable cyclic orthocarboxylic acid esters are 1,4-dimethyl-3,5,8-trioxabicyclo[2.2.2]octane and 4-ethyl-1-methyl-3,5,8-trioxabicyclo[2.2.2]octane.

Examples of acyclic esters of carboxylic acids are ethyl and methyl formiate, ethyl and methyl acetate, ethyl and methyl proprionate, and ethyl and methyl butanoate, and esters of dicarboxylic acids like 1,3-dimethyl propanedioate. An example of a cyclic ester of carboxylic acids (lactones) is γ-butyrolactone.

Examples of cyclic and acyclic sulfones are ethyl methyl sulfone, dimethyl sulfone, and tetrahydrothiophene-S,S-dioxide (sulfolane).

Examples of cyclic and acyclic nitriles and dinitriles are adipodinitrile, acetonitrile, propionitrile, and butyronitrile.

The inventive electrolyte composition usually contains at least one conducting salt. The electrolyte composition functions as a medium that transfers ions participating in the electrochemical reaction taking place in an electrochemical cell. The conducting salt(s) present in the electrolyte are usually solvated in the aprotic organic solvent(s). Preferably the conducting salt is a lithium conducting salt. The conducting salt is preferably selected from the group consisting of

- $Li[F_{6-x}P(C_yF_{2y+1})_x]$, wherein x is an integer in the range from 0 to 6 and y is an integer in the range from 1 to 20;
  $Li[B(R^I)_4]$, $Li[B(R^I)_2(OR^{II}O)]$ and $Li[B(OR^{II}O)_2]$ wherein each R^I is independently from each other selected from F, Cl, Br, I, C_1-C_4 alkyl, C_2-C_4 alkenyl, C_2-C_4 alkynyl, OC_1-C_4 alkyl, OC_2-C_4 alkenyl, and OC_2-C_4 alkynyl wherein alkyl, alkenyl, and alkynyl may be substituted by one or more OR^{III}, wherein R^{III} is selected from C_1-C_6 alkyl, C_2-C_6 alkenyl, and C_2-C_6 alkynyl, and
  $(OR^{II}O)$ is a bivalent group derived from a 1,2- or 1,3-diol, a 1,2- or 1,3-dicarboxlic acid or a 1,2- or 1,3-hydroxycarboxylic acid, wherein the bivalent group forms a 5- or 6-membered cycle via the both oxygen atoms with the central B-atom;
- $LiClO_4$; $LiAsF_6$; $LiCF_3SO_3$; Li_2SiF_6; $LiSbF_6$; $LiAlCl_4$, $Li(N(SO_2F)_2)$, lithium tetrafluoro (oxalato) phosphate; lithium oxalate; and
- salts of the general formula $Li[Z(C_nF_{2n+1}SO_2)_m]$, where m and n are defined as follows:
  m = 1 when Z is selected from oxygen and sulfur,
  m = 2 when Z is selected from nitrogen and phosphorus,
  m = 3 when Z is selected from carbon and silicon, and
  n is an integer in the range from 1 to 20.

Suited 1,2- and 1,3-diols from which the bivalent group $(OR^{II}O)$ is derived may be aliphatic or aromatic and may be selected, e.g., from 1,2-dihydroxybenzene, propane-1,2-diol, butane-1,2-diol, propane-1,3-diol, butan-1,3-diol, cyclohexyl-trans-1,2-diol and naphthalene-2,3-diol which are optionally are substituted by one or more F and/or by at least one straight or branched non fluorinated, partly fluorinated or fully fluorinated C_1-C_4 alkyl group. An example for such 1,2- or 1,3-diole is 1,1,2,2-tetra(trifluoromethyl)-1,2-ethane diol.

“Fully fluorinated C_1-C_4 alkyl group” means, that all H-atoms of the alkyl group are substituted by F.

Suited 1,2- or 1,3-dicarboxlic acids from which the bivalent group $(OR^{II}O)$ is derived may be aliphatic or aromatic, for example oxalic acid, malonic acid (propane-1,3-dicarboxylic acid), phthalic acid or isophthalic acid, preferred is oxalic acid. The 1,2- or 1,3-dicarboxlic acid are optionally substituted by one or more F and/or by at least one straight or branched non fluorinated, partly fluorinated or fully fluorinated C_1-C_4 alkyl group.

Suited 1,2- or 1,3-hydroxycarboxylic acids from which the bivalent group ($OR^{II}O$) is derived may be aliphatic or aromatic, for example salicylic acid, tetrahydro salicylic acid, malic acid, and 2-hydroxy acetic acid, which are optionally substituted by one or more F and/or by at least one straight or branched non fluorinated, partly fluorinated or fully fluorinated C_1-C_4 alkyl group. An example for such 1,2- or 1,3-hydroxycarboxylic acids is 2,2-bis(trifluoromethyl)-2-hydroxy-acetic acid.

Examples of $Li[B(R^I)_4]$, $Li[B(R^I)_2(OR^{II}O)]$ and $Li[B(OR^{II}O)_2]$ are $LiBF_4$, lithium difluoro oxalato borate and lithium dioxalato borate.

Preferably the at least one conducting salt (ii) is selected from $Li[N(FSO_2)_2]$, $Li[N(CF_3SO_2)_2]$, $LiClO_4$, $LiPF_6$, $LiBF_4$, and $LiPF_3(CF_2CF_3)_3$, more preferred the conducting salt (ii) is selected from $LiPF_6$ and $LiBF_4$, and the most preferred conducting salt (ii) is $LiPF_6$.

The at least one conducting salt is usually present at a minimum concentration of at least 0.1 mol/l, preferably the concentration of the at least one conducting salt is 0.5 to 2 mol/l based on the entire electrolyte composition.

The electrolyte composition according to the present invention may contain at least one further additive different from the compounds of formula (I) and formula (II). The further additive may be selected from polymers, SEI forming additives, flame retardants, overcharge protection additives, wetting agents, HF and/or H_2O scavenger, stabilizer for $LiPF_6$ salt, ionic salvation enhancer, corrosion inhibitors, gelling agents, and the like.

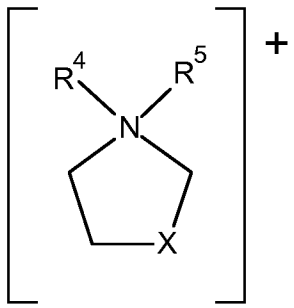
Examples for polymers used in electrolyte compositions are polyvinylidene fluoride, polyvinylidene-hexafluoropropylene copolymers, polyvinylidene-hexafluoropropylene-chlorotrifluoroethylene copolymers, Nafion, polyethylene oxide, polymethyl methacrylate, polyacrylonitrile, polypropylene, polystyrene, polybutadiene, polyethylene glycol, polyvinylpyrrolidone, polyaniline, polypyrrole and/or polythiophene. These polymers may be added to electrolyte compositions containing a solvent or solvent mixture in order to convert liquid electrolytes into quasi-solid or solid electrolytes and thus to improve solvent retention, especially during ageing.

Examples of flame retardants are organic phosphorous compounds like cyclophosphazenes, phosphoramides, alkyl and/or aryl tri-substituted phosphates, alkyl and/or aryl di- or tri-substituted phosphites, alkyl and/or aryl di- substituted phosphonates, alkyl and/or aryl tri-substituted phosphines, and fluorinated derivatives thereof.

Examples of HF and/or H_2O scavenger are optionally halogenated cyclic and acyclic silylamines.

Examples of overcharge protection additives are cyclohexylbenzene, o-terphenyl, p-terphenyl, and biphenyl and the like, preferred are cyclohexylbenzene and biphenyl.

Examples of SEI forming additives are vinylene carbonate and its derivatives such as vinylene carbonate and methylvinylene carbonate; fluorinated ethylene carbonate and its derivatives such as monofluoroethylene carbonate, cis- and trans-difluorocarbonate; propane sultone and its derivatives; ethylene sulfite and its derivatives; oxalate comprising compounds such as lithium oxalate, oxalato borates including dimethyl oxalate, lithium bis(oxalate) borate, lithium difluoro (oxalato) borate, and ammonium bis(oxalato) borate, and oxalato phosphates including lithium tetrafluoro (oxalato) phosphate; lithium fluorophosphates including $LiPO_2F_2$; and ionic compounds of formula (III) K^+A^- containing a cation K^+ of formula (IIIa)



(IIIa)

wherein
X is CH_2 or NR^a,
R^4 is selected from C_1 to C_6 alkyl,
R^5 is selected from $-(CH_2)_u-SO_3-(CH_2)_v-R^b$,
$-SO_3-$ is $-O-S(O)_2-$ or $-S(O)_2-O-$, preferably $-SO_3-$ is $-O-S(O)_2-$,
u is an integer from 1 to 8, preferably u is 2, 3 or 4, wherein one or more CH_2 groups of the $-(CH_2)_u-$ alkylene chain which are not directly bound to the N-atom and/or the SO_3 group may be replaced by O and wherein two adjacent CH_2 groups of the $-(CH_2)_u-$ alkylene chain may be replaced by a C-C double bond, preferably the $-(CH_2)_u-$ alkylene chain is not substituted and u
u is an integer from 1 to 8, preferably u is 2, 3 or 4,
v is an integer from 1 to 4, preferably v is 0,
R^a is selected from C_1 to C_6 alkyl,
R^b is selected from C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_6-C_{12} aryl, and C_6-C_{24} aralkyl, which may contain one or more F, and wherein one or more CH_2 groups of alkyl, alkenyl, alkynyl and aralkyl which are not directly bound to the SO_3 group may be replaced by O, preferably R^b is selected from C_1-C_6 alkyl, C_2-C_4 alkenyl, and C_2-C_4 alkynyl, which may contain one or more F, and wherein one or more CH_2 groups of alkyl, alkenyl, alkynyl and aralkyl which are not directly bound to the SO_3 group may be replaced by O, preferred examples of R^b include methyl, ethyl, trifluoromethyl, pentafluoroethyl, n-propyl, n-butyl, n-hexyl, ethenyl, ethynyl, allyl or prop-1-yn-yl,
and an anion A^- selected from bisoxalato borate, difluoro (oxalato) borate, $[F_zB(C_mF_{2m+1})_{4-z}]^-$, $[F_yP(C_mF_{2m+1})_{6-y}]^-$, $(C_mF_{2m+1})_2P(O)O]^-$, $[C_mF_{2m+1}P(O)O_2]^{2-}$, $[O-C(O)-C_mF_{2m+1}]^-$, $[O-S(O)_2-C_mF_{2m+1}]^-$, $[N(C(O)-C_mF_{2m+1})_2]^-$, $[N(S(O)_2-C_mF_{2m+1})_2]^-$, $[N(C(O)-C_mF_{2m+1})(S(O)_2-C_mF_{2m+1})]^-$, [N(C(O)-

$C_mF_{2m+1})(C(O)F)]^-$, $[N(S(O)_2\text{-}C_mF_{2m+1})(S(O)_2F)]^-$, $[N(S(O)_2F)_2]^-$, $[C(C(O)\text{-}C_mF_{2m+1})_3]^-$, $[C(S(O)_2\text{-}C_mF_{2m+1})_3]^-$, wherein m is an integer from 1 to 8, z is an integer from 1 to 4, and y is an integer from 1 to 6,

Preferred anions A^- are bisoxalato borate, difluoro (oxalato) borate, $[F_3B(CF_3)]^-$, $[F_3B(C_2F_5)]^-$, $[PF_6]^-$, $[F_3P(C_2F_5)_3]^-$, $[F_3P(C_3F_7)_3]^-$, $[F_3P(C_4F_9)_3]^-$, $[F_4P(C_2F_5)_2]^-$, $[F_4P(C_3F_7)_2]^-$, $[F_4P(C_4F_9)_2]^-$, $[F_5P(C_2F_5)]^-$, $[F_5P(C_3F_7)]^-$ or $[F_5P(C_4F_9)]^-$, $[(C_2F_5)_2P(O)O]^-$, $[(C_3F_7)_2P(O)O]^-$ or $[(C_4F_9)_2P(O)O]^-$. $[C_2F_5P(O)O_2]^{2-}$, $[C_3F_7P(O)O_2]^{2-}$, $[C_4F_9P(O)O_2]^{2-}$, $[O\text{-}C(O)CF_3]^-$, $[O\text{-}C(O)C_2F_5]^-$, $[O\text{-}C(O)C_4F_9]^-$, $[O\text{-}S(O)_2CF_3]^-$, $[O\text{-}S(O)_2C_2F_5]^-$, $[N(C(O)C_2F_5)_2]^-$, $[N(C(O)(CF_3)_2]^-$, $[N(S(O)_2CF_3)_2]^-$, $[N(S(O)_2C_2F_5)_2]^-$, $[N(S(O)_2C_3F_7)_2]^-$, $[N(S(O)_2CF_3)\ (S(O)_2C_2F_5)]^-$, $[N(S(O)_2C_4F_9)_2]^-$, $[N(C(O)CF_3)(S(O)_2CF_3)]^-$, $[N(C(O)C_2F_5)(S(O)_2CF_3)]^-$ or $[N(C(O)CF_3)(S(O)_2\text{-}C_4F_9)]^-$, $[N(C(O)CF_3)(C(O)F)]^-$, $[N(C(O)C_2F_5)(C(O)F)]^-$, $[N(C(O)C_3F_7)(C(O)F)]^-$, $[N(S(O)_2CF_3)(S(O)_2F)]^-$, $[N(S(O)_2C_2F_5)(S(O)_2F)]^-$, $[N(S(O)_2C_4F_9)(S(O)_2F)]^-$, $[C(C(O)CF_3)_3]^-$, $[C(C(O)C_2F_5)_3]^-$ or $[C(C(O)C_3F_7)_3]^-$, $[C(S(O)_2CF_3)_3]^-$, $[C(S(O)_2C_2F_5)_3]^-$, and $[C(S(O)_2C_4F_9)_3]^-$.

More preferred the anion is selected from bisoxalato borate, difluoro (oxalato) borate, $CF_3SO_3^-$, and $[PF_3(C_2F_5)_3]^-$.

Preferred SEI-forming additives are oxalato borates, fluorinated ethylene carbonate and its derivatives, vinylene carbonate and its derivatives, and compounds of formula (III). More preferred are lithium bis(oxalato) borate (LiBOB), lithium fluorophosphates (e.g. $LiPO_2F_2$) vinylene carbonate, monofluoro ethylene carbonate, and compounds of formula (III), in particular monofluoro ethylene carbonate, and compounds of formula (III).

A compound added as additive may have more than one effect in the electrolyte composition and the device comprising the electrolyte composition. E.g. lithium oxalato borate may be added as additive enhancing the SEI formation but it may also be added as conducting salt.

In case one or more further additives are present, the total concentration of all further additives is at least 0.05 wt.-%, based on the total amount of the electrolyte composition, preferred the total concentration of the one or more further additives is 0.1 to 30 wt.-%, more preferred 0.5 to 10 wt.-%.

According to one embodiment of the present invention the electrolyte composition contains at least one compound of formula (I), at least one compound of formula (II), and at least one SEI forming additive, all as described above or as described as being preferred.

In one embodiment of the present invention, the electrolyte composition contains:

(i) at least one compound of formula (I) and at least one compound of formula (II),
(ii) at least one organic aprotic solvent,
(iii) at least one conducting salt, and
(iv) optionally at least one further additive different from the compounds of formula (I) and (II).

The electrolyte composition preferably contains

(i) in total 0.005 to 10 wt.-% of compound(s) of formula (I) and (II), prefered 0.01 to 6 wt.-%, even more prefered 0.05 to 5 wt.-%,
(ii) in total 60 to 99.9 wt.-% of organic aprotic solvent(s),
(iii) at minimum 0.1 mol/l of at least one conducting salt, preferably 0.5 to 2 mol/l, and
(iv) zero to in total 30 wt.-% of further additive(s) different from the compounds of formula (I) and (II), preferably in total 0.1 to 30 wt.-%, even more preferred in total 0.5 to 10 wt.-%,

based on the total amount of the electrolyte composition.

The inventive electrolyte composition is preferably liquid at working conditions; more preferred it is liquid at 1 bar and 25 °C, even more preferred the electrolyte composition is liquid at 1 bar and -15 °C.

The water content of the inventive electrolyte composition is preferably below 100 ppm, based on the weight of the electrolyte composition, more preferred below 50 ppm, most preferred below 30 ppm. The water content may be determined by titration according to Karl Fischer, e.g. described in detail in DIN 51777 or ISO760: 1978.

The content of HF of the inventive electrolyte composition is preferably below 200 ppm, based on the weight of the electrolyte composition, more preferred below 100 ppm, most preferred below 60 ppm. The HF content may be determined by titration according to potentiometric or potentiographic titration method.

The electrolyte compositions of the invention are prepared by methods which are known to the person skilled in the field of the production of electrolytes, generally by dissolving a conductiing salt in the corresponding solvent mixture and adding the compounds of the formula (I) and formula (II) according to the invention and optionally additional additives, as described above.

The electrolyte compositions are used in electrochemical cells like secondary lithium batteries, double layer capacitors, and lithium ion capacitors, preferably the inventive electrolyte compositions are used in secondary lithium batteries and more preferred in lithium ion batteries.

Another object of the present invention is an electrochemical cell comprising the electrolyte composition as described above.

The general construction of such electrochemical devices is known and is familiar to the person skilled in this art – for batteries, for example, in Linden's Handbook of Batteries (ISBN 978-0-07-162421-3).

The inventive electrochemical cell may be a secondary lithium battery, a double layer capacitor, or a lithium ion capacitor. Preferably the electrochemical cell is a secondary lithium battery. The term “secondary lithium battery” as used herein means a secondary electrochemical cell, wherein the anode comprises lithium metal or lithium ions sometime during the charge/discharge of the cell. The anode may comprise lithium metal or a lithium metal alloy, a material occluding and releasing lithium ions, or other lithium containing compounds; e.g. the lithium battery may be a lithium ion battery, a lithium/sulphur battery, or a lithium/selenium sulphur battery.

In particular preferred the electrochemical device is a lithium ion battery, i.e. a secondary lithium ion electrochemical cell comprising a cathode comprising a cathode active material that can reversibly occlude and release lithium ions and an anode comprising an anode active material that can reversibly occlude and release lithium ions. The terms “secondary lithium ion electrochemical cell” and “(secondary) lithium ion battery” are used interchangeably within the present invention.

The at least one cathode active material preferably comprises a material capable of occluding and releasing lithium ions selected from lithium transition metal phosphates and lithium intercalating metal oxides. The lithium is usually intercalated in form of lithium ions.

Examples of lithium transition metal phosphates are $LiFePO_4$ and $LiCoPO_4$, examples of lithium intercalating metal oxides are $LiCoO_2$, $LiNiO_2$, mixed transition metal oxides with layer structure having the general formula $Li_{(1+z)}[Ni_aCo_bMn_c]_{(1-z)}O_{2+e}$ wherein z is 0 to 0.3; a, b and c may be same or different and are independently 0 to 0.8 wherein a + b + c = 1; and $-0.1 \leq e \leq 0.1$, and manganese-containing spinels like $LiMnO_4$ and spinels of general formula $Li_{1+t}M_{2-t}O_{4-d}$ wherein d is 0 to 0.4, t is 0 to 0.4 and M is Mn and at least one further metal selected from the group consisting of Co and Ni, and $Li_{(1+g)}[Ni_hCo_iAl_j]_{(1-g)}O_{2+k}$. Typical values for g, h, l, j and k are: g = 0, h = 0.8 to 0.85, i = 0.15 to 0.20, j = 0.02 to 0.03 and k = 0.

The cathode may further comprise electrically conductive materials like electrically conductive carbon and usual components like binders. Compounds suited as electrically conductive materials and binders are known to the person skilled in the art. For example, the cathode may comprise carbon in a conductive polymorph, for example selected from graphite, carbon black, carbon nanotubes, graphene or mixtures of at least two of the aforementioned substances. In addition, the cathode may comprise one or more binders, for example one or more organic polymers like polyethylene, polyacrylonitrile, polybutadiene, polypropylene, polystyrene, polyacrylates, polyvinyl alcohol, polyisoprene and copolymers of at least two comonomers selected from ethylene, propylene, styrene, (meth)acrylonitrile and 1,3-butadiene, especially styrene-butadiene copolymers, and halogenated (co)polymers like polyvinlyidene chloride, polyvinly chloride, polyvinyl fluoride, polyvinylidene fluoride (PVdF), polytetrafluoroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, copolymers of tetrafluoroethylene and vinylidene fluoride and polyacrylnitrile.

The anode comprised within the lithium batteries of the present invention comprises an anode active material that can reversibly occlude and release lithium ions or is capable to form an alloy with lithium. In particular carbonaceous material that can reversibly occlude and release lithium ions can be used as anode active material. Carbonaceous materials suited are crystalline carbon such as a graphite material, more particularly, natural graphite, graphitized cokes, graphitized MCMB, and graphitized MPCF; amorphous carbon such as coke, mesocarbon microbeads (MCMB) fired below 1500°C, and mesophase pitch-based carbon fiber (MPCF); hard carbon and carbonic anode active material (thermally decomposed carbon, coke, graphite) such as a carbon composite, combusted organic polymer, and carbon fiber.

Further anode active materials are lithium metal, or materials containing an element capable of forming an alloy with lithium. Non-limiting examples of materials containing an element capable of forming an alloy with lithium include a metal, a semimetal, or an alloy thereof. It should be understood that the term “alloy” as used herein refers to both alloys of two or more metals as well as alloys of one or more metals together with one or more semimetals. If an alloy has metallic properties as a whole, the alloy may contain a nonmetal element. In the texture of the alloy, a solid solution, a eutectic (eutectic mixture), an intermetallic compound or two or more thereof coexist. Examples of such metal or semimetal elements include, without being limited to, titanium (Ti), tin (Sn), lead (Pb), aluminum, indium (In), zinc (Zn), antimony (Sb), bismuth (Bi), gallium (Ga), germanium (Ge), arsenic (As), silver (Ag), hafnium (Hf), zirconium (Zr) yttrium (Y), and silicon (Si). Metal and semimetal elements of Group 4 or 14 in the long-form periodic table of the elements are preferable, and especially preferable are titanium, silicon and tin, in particular silicon. Examples of tin alloys include ones having, as a second constituent element other than tin, one or more elements selected from the group consisting of silicon, magnesium (Mg), nickel, copper, iron, cobalt, manganese, zinc, indium, silver, titanium (Ti), germanium, bismuth, antimony and chromium (Cr). Examples of silicon alloys include ones having, as a second constituent element other than silicon, one or more elements selected from the group consisting of tin, magnesium, nickel, copper, iron, cobalt, manganese, zinc, indium, silver, titanium, germanium, bismuth, antimony and chromium.

A further possible anode active material is silicon which is able to intercalate lithium ions. The silicon may be used in different forms, e.g. in the form of nanowires, nanotubes, nanoparticles, films, nanoporous silicon or silicon nanotubes. The silicon may be deposited on a current collector. The current collector may be a metal wire, a metal grid, a metal web, a metal sheet, a metal foil or a metal plate. Preferred the current collector is a metal foil, e.g. a copper foil. Thin films of silicon may be deposited on metal foils by any technique known to the person skilled in the art, e.g. by sputtering techniques. One possibility of preparing Si thin film electrodes are described in R. Elazari et al.; Electrochem. Comm. 2012, 14, 21-24. It is also possible to use a silicon/carbon mixture as anode active material according to the present invention.

Other possible anode active materials are lithium ion intercalating oxides of Ti.

Preferably the anode active material is selected from carbonaceous material that can reversibly occlude and release lithium ions, particularly preferred the carbonaceous material that can reversibly occlude and release lithium ions is selected from crystalline carbon, hard carbon and amorphous carbon, in particular preferred is graphite. In another preferred embodiment the anode active is selected from silicon that can reversibly occlude and release lithium ions, preferably the anode comprises a thin film of silicon or a silicon/carbon mixture. In a further preferred embodiment the anode active is selected from lithium ion intercalating oxides of Ti.

The anode and cathode may be made by preparing an electrode slurry composition by dispersing the electrode active material, a binder, optionally a conductive material and a thickener, if desired, in a solvent and coating the slurry composition onto a current collector. The current collector may be a metal wire, a metal grid, a metal web, a metal sheet, a metal foil or a metal plate. Preferred the current collector is a metal foil, e.g. a copper foil or aluminum foil.

The inventive lithium batteries may contain further constituents customary per se, for example separators, housings, cable connections etc. The housing may be of any shape, for example cuboidal or in the shape of a cylinder, the shape of a prism or the housing used is a metal-plastic composite film processed as a pouch. Suited separators are for example glass fiber separators and polymer-based separators like polyolefin separators.
Several inventive lithium batteries may be combined with one another, for example in series connection or in parallel connection. Series connection is preferred. The present invention further provides for the use of inventive lithium ion batteries as described above in devices, especially in mobile devices. Examples of mobile devices are vehicles, for example automobiles, bicycles, aircraft, or water vehicles such as boats or ships. Other examples of mobile devices are those which are portable, for example computers, especially laptops, telephones or electrical power tools, for example from the construction sector, especially drills, battery-driven screwdrivers or battery-driven tackers. But the inventive lithium ion batteries can also be used for stationary energy stores.

Even without further statements, it is assumed that a skilled person is able to utilize the above description in its widest extent. Consequently, the preferred embodiments and examples are to be interpreted merely as a descriptive enclosure which in no way has any limiting effect at all.

The invention is illustrated by the examples which follow, which do not, however, restrict the invention.

1. Electrolyte compositions

Electrolyte compositions were prepared from ethylene carbonate (EC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), monofluoroethylene carbonate (FEC), 1H,1H,5H-perfluoropentyl-1,1,2,2-tetrafluoroethylether (PF1), vinylene carbonate (VC), propane sultone (PS), $LiPF_6$,

$LiBF_4$, adiponitrile, succinonitrile, and 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile (compound (I.1)).. The compositions are indicated in Table 1.

2. Electrochemical cells.

Commercially available wound pouch dry cells with a nominal capacity of 250 mAh (lithium cobalt oxide vs graphite, the lithium cobalt oxide was used in in form of particles coated with aluminium oxide for the preparation of the cell) were dried at 70°C *in vacuo* for 24h. Then the cells were filled with 700 µl electrolyte under Argon atmosphere. After 5h rest at room temperature the cells were evacuated and sealed. The cells were then cycled between 2.75 and 4.4V for 5 cycles, charged to 4.4V and stored at 85°C for 24h. The resistance of the cells was measured before and after storage using a 1kHz ACImp device and a 10s constant current pulse. The volume change of the cells was measured before and after 85°C storage by using Archimedes' principle. This method is known to those skilled in the art. The results of the experiments are shown in Table 1.

Table 1:

	Electrolyte formulation	Δvolume [%]	Voltage drop [mV]	ΔDCIR [mOhm]	ΔACImp [mOhm]
Comp. example 1	EC:EMC 3:7 w:w 1MLiPF$_6$ + 0.5 wt.-% compound (I.1)	3.7	114	367	87
Comp. example 2	EC:EMC 3:7 w:w 1MLiPF$_6$ + 0.34 wt.-% adiponitrile	4.6	116	358	27
Example 1	EC:EMC 3:7 w:w 1MLiPF$_6$ + 0.5 wt.-% compound (I.1) + 0.34 wt.-% adiponitrile	4.6	113	254	30
Comp. example 3	EC:DEC 3:7 vol 1.1 MLiPF$_6$ + 2.5 wt.-% VC + 0.15 wt.-% LiBF$_4$ + 1.75 wt.-%FEC + 0.5 wt-% adiponitrile	3.2	83	535	20
Example 2	EC:DEC 3:7 vol 1.1 MLiPF$_6$ + 2.5 wt.-% VC + 0.15 wt.-% LiBF$_4$ + 1.75 wt.-%FEC + 0.5 wt-% adiponitrile + 0.1 wt.-% compound (I.1)	2.6	77	499	16
Example 3	EC:DEC 3:7 vol 1.1 MLiPF$_6$ + 2.5 wt.-% VC + 0.15 wt.-% LiBF$_4$ + 1.75 wt.-%FEC + 0.1 wt.-% adiponitrile + 0.1 wt.-% compound (I.1)	2.3	77	487	16
Comp. example 4	EC:EMC:DEC 20:50:30 w:w 1.15 M LiPF$_6$ +1 wt.-% VC + 2 wt.-% PS + 6.5 wt.-% FEC + 5 wt.-% PF1 + 1.5 wt.-% Succinonitrile	11.0	123	702	36
Example 4	EC:EMC:DEC 20:50:30 w:w 1.15M LiPF$_6$ +1 wt.-% VC + 2 wt.-% PS + 6.5 wt.-% FEC + 5 wt.-% PF1 + 1.5 wt.-% Succinonitrile + 0.1 wt.-% compound (I.1)	9.4	115	539	31
Example 5	EC:EMC:DEC 20:50:30 w:w 1.15M LiPF$_6$ +1 wt.-% VC + 2 wt.-% PS + 6.5 wt.-% FEC + 5 wt.-% PF1 + 1.5 wt.-% Succinonitrile + 0.5 wt.-% compound (I.1)	8.6	97	514	24

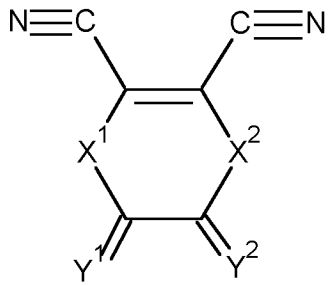
Δ volume: Change in the cell volume after 85°C storage.
Voltage drop: Change in the open circuit potential of the cells after 85°C storage.
Δ DCIR: Change in the DCIR resistance after 85°C storage.
Δ ACImp: Change in the 1kHz AC Impedance resistance after 85°C storage.

The comparison of example 1 with comparative examples 1 and 2 shows a synergistic effect of the combination of the linear dinitrile adiponitrile and the cyclic dinitrile of formula (I.1) in respect of the reduction of the internal resistance of the cell when it is subjected to a current pulse (DCIR). The reduction of the internal resistance is not a mere concentration effect as can be seen from comparison of comparative example 3 with examples 2 and 3 and the comparison of comparative example 4 with examples 4 and 5.

All inventive examples exhibit similar or lower gas evolution (Δvolume) than the respective comparative examples.

Claims

1. An electrolyte composition containing at least one compound of formula (I)



(I)

wherein

X^1 and X^2 are independently from each other selected from $N(R^1)$, $P(R^1)$, O, and S;

R^1 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_{10} alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^3, $C(O)R^3$, $C(NR^3)R^4$, and $C(O)OR^3$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3a}$, $OS(O)_2R^{3a}$, $S(O)_2R^{3a}$, OR^{3a}, $C(O)R^{3a}$, $C(O)OR^{3a}$, $NR^{3a}R^{3b}$, and $NC(O)R^{3a}R^{3b}$;

Y^1 and Y^2 are independently from each other selected from (O), (S), (PR^2) and (NR^2),

R^2 is selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, C_6-C_{13} (hetero)aralkyl, OR^{2a} and $C(O)R^{2a}$, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{2b}$, $OS(O)_2R^{2b}$, $S(O)_2R^{2b}$, OR^{2b}, $C(O)R^{2b}$, $C(O)OR^{2b}$, $NR^{2b}R^{2c}$, and $NC(O)R^{2b}R^{2c}$; and

R^{2a}, R^{2b} and R^{2c} are independently from each other selected from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl, (hetero)cycloalkyl, alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN,

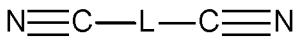
R^3, R^4, R^{3a}, and R^{3b} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, C_3-C_6 (hetero)cycloalkenyl, C_2-C_6 alkynyl, C_5-C_7 (hetero)aryl, and C_6-C_{13} (hetero)aralkyl, wherein alkyl, (hetero)cycloalkyl, alkenyl, (hetero)cycloalkenyl, alkynyl, (hetero)aryl, and (hetero)aralkyl may be substituted by one or more substituents selected from F, CN, C_1-C_6 alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_6 alkenyl, C_5-C_7 (hetero)aryl, $S(O)_2OR^{3c}$, $OS(O)_2R^{3c}$, $S(O)_2R^{3c}$, OR^{3c}, $C(O)R^{3c}$, $C(O)OR^{3c}$, $NR^{3c}R^{3d}$, and $NC(O)R^{3c}R^{3d}$; and

R^{3c} and R^{3d} are selected independently from each other from H, C_1-C_{10} alkyl, C_3-C_6 (hetero)cycloalkyl, C_2-C_{10} alkenyl, and C_5-C_7 (hetero)aryl, wherein alkyl,

(hetero)cycloalkyl, alkenyl, and (hetero)aryl may be substituted by one or more substituents selected from F and CN;

and

at least one compound of formula (II)



(II)

wherein

L is a $–(CH_2)_n–$ chain wherein one or more CH_2 groups of the $–(CH_2)_n–$ chain which are not directly bound to a CN group may be replaced by O, S or $N(R^5)$ and wherein a C-C single bond between two adjacent CH_2 groups of the $–(CH_2)_n–$chain may be replaced by a C-C double bond or a C-C triple bond and wherein one or more H of the $–(CH_2)_n–$chain may be substituted independently from each other by F, NR^6R^6, SR^6, OR^6 and/or optionally fluorinated C_1-C_{10} alkyl and wherein two H of a (CH_2) group of the $–(CH_2)_n–$chain may be substituted by $=C(R^6R^7)$;

n is an integer from 1 to 12;

R^5, R^6 and R^7 are independently from each other selected from H and optionally fluorinated C_1-C_6 alkyl.

2. The electrolyte composition according to claim 1, wherein X^1 and X^2 are independently from each other selected from $N(R^1)$.

3. The electrolyte composition according to claim 1 or 2, wherein Y^1 and Y^2 are (O).

4. The electrolyte composition according to any of claims 1 to 3, wherein L is a $–(CH_2)_n–$ chain wherein one or more CH_2 groups of the $–(CH_2)_n–$ chain which are not directly bound to a CN group may be replaced by O or S and wherein a C-C single bond between two adjacent CH_2 groups of the $–(CH_2)_n–$chain may be replaced by a C-C double bond or a C-C triple bond and wherein one or more H of the $–(CH_2)_n–$chain may be substituted independently from each other by F and optionally fluorinated C_1-C_4 alkyl and wherein two H of a (CH_2) group of the $–(CH_2)_n–$chain may be substituted by $=C(R^6R^7)$ with R^6 and R^7 are selected independently from H and optionally fluorinated C_1-C_4 alkyl; and n is an integer from 1 to 10.

5. The electrolyte composition according to any of claims 1 to 4, wherein n is an integer from 2 to 10.

6. The electrolyte composition according any of claims 1 to 5, wherein the at least one compound of formula (II) is selected from adipodinitrile, succinodinitrile, trans-3-hexenedinitrile, 2- hexenedinitrile, dodecanedinitrile, suberonitrile, pimelonitrile, subeconitrile, azelanitrile, glutaronitrile, 2-methlyeneglutaronitrile, 2-methylglutaronitrile, 2-methyladiponitrile, 2-methylsuccinonitrile, 2-methylsuberonitrile, 2-methylazelanitrile, 2,2-

dimethylglutaronitrile, 2,2-dimethyladiponitrile, 2,2-dimethylsuberonitrile, 2,2-dimethylazelanitrile, 2,2-dimethylsuccinonitrile, 2,2,4,4-tetramethylglutaronitrile, 2,2,4,4-tetramethylsuccinonitrile, 2,2,4,4-tetramethyladiponitrile, 2,2,4,4-tetramethylsuberonitrile, 2,2,4,4-tetramethylazelanitrile, 3-[2-(2-cyanoethoxy)ethoxy]propanenitrile, 3-(2-cyanoethoxy)propanenitrile and 3,3'-thiodipropiodinitrile.

7. The electrolyte composition according to any of claims 1 to 6, wherein the molar ratio of compound(s) of formula (I) and compound(s) of formula (II) is in the range of from 1 : 99 to 99 : 1.

8. The electrolyte composition according to any of claims 1 to 7, wherein the total concentration of compounds of formula (I) and formula (II) in the electrolyte composition is in the range of 0.005 to 10 wt.-% of the total amount of the electrolyte composition.

9. The electrolyte composition according to any of claims 1 to 8, wherein the electrolyte composition contains at least one aprotic organic solvent.

10. The electrolyte composition according to any of claims 1 to 9, wherein the electrolyte composition contains at least one aprotic organic solvent selected from cyclic and linear carbonates.

11. The electrolyte composition according to any of claims 1 to 10, wherein the electrolyte composition contains at least one lithium conducting salt.

12. The electrolyte composition according to any of claims 1 to 11, wherein the electrolyte composition contains at least one additive different from the compounds of formula (I) and formula (II).

13. An electrochemical cell comprising the electrolyte composition according to any of claims 1 to 12.

14. The electrochemical cell according to claim 13 wherein the electrochemical cell is a secondary lithium battery.

15. The electrochemical cell according to claim 14 wherein the electrochemical cell comprises a cathode containing at least one cathode active material selected from lithium intercalating transition metal oxides and lithium transition metal phosphates.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/061375

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M10/0525 H01M10/0567 H01M10/0568
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, EMBASE, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/007554 A1 (BASF SE [DE]) 22 January 2015 (2015-01-22) cited in the application claims 1-15	1-15
A	EP 2 683 015 A1 (LG CHEMICAL LTD [KR]) 8 January 2014 (2014-01-08) paragraph [0020] - paragraph [0027]; claims 1-15	1-15
A	WO 2015/033620 A1 (ISHIHARA SANGYO KAISHA [JP]) 12 March 2015 (2015-03-12) claim 10	1-15
A	US 2008/220336 A1 (MUN IN-TAE [KR] ET AL) 11 September 2008 (2008-09-11) claims 1-43	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2016	14/07/2016

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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