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(54) Title: FLUORINATED PEROXIDES, THEIR USE AS ELECTROLYTE COMPONENT AND PROCESS FOR THEIR PREPARATION

(57) Abstract: The present invention concerns compounds of formula R1-O-O-R2 (Formula (I)) wherein R1 and R2 are perfluorinated or partially fluorinated branched or linear alkyl, their use as electrolyte component and processes for their preparation.



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FLUORINATED PEROXIDES, THEIR USE AS ELECTROLYTE COMPONENT AND
PROCESS FOR THEIR PREPARATION

The present invention relates to the technical field of batteries. More specifically it
5 concerns perfluorinated or partially fluorinated peroxides, their use as electrolyte component
and a process for the preparation of such compounds.

Background of the invention

In the field of battery, it is advantageous to have a liquid electrolyte component which
10 is stable at high temperature and which can be preferably compatible with high voltage
batteries.

The development of new compounds which are more stable, and could be used as
electrolyte component is therefore of particular interest.

Fluorinated peroxides are mainly known as gas. For example $\text{CF}_3\text{-O-O-CF}_3$ has been
15 described in WO 2014/096414 as alternative to SF_6 and N_2 as dielectric insulating gas.
Besides, many chemical compounds have been disclosed as component in electrolyte for
batteries: fluorinated carbonates (see for instance US 2016/0118690), metallic organic acid
peroxide salts of general formula R-C(O)-O-OM^+ (see for instance WO 2014/016271),
fluorinated methoxymalonic acid esters (see for instance WO 2013/174697). However the use
20 of such fluorinated peroxides in the battery field has never been suggested.

The object of the present invention is to provide new fluorinated or partially
fluorinated compounds which are useful as electrolyte component. This object and other
objects are achieved by this invention. Advantageously the compounds of the present
25 invention are liquid at normal temperature and pressure. Additionally the polarity of the
compounds of the present invention is tunable in order to adjust their solubility properties.
Eventually the compounds of the present invention can also be destroyed at very high voltage
in order to contribute to the surface electrolyte interface, and thus improve the cycle life of
battery.

Brief description of the invention

Accordingly a first aspect of the present invention concerns a compound of formula R1-O-O-R2 (Formula (I)) wherein R1 is C(CF₃)₃ and R2 is a perfluorinated or partially fluorinated linear or branched alkyl and wherein R2 is different from R1.

5 In another aspect, the present invention concerns the use of at least one compound of formula (I) R1-O-O-R2 as electrolyte component wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

In a further aspect, the present invention concerns an electrolyte composition for an electrochemical device comprising at least one compound of formula (I) R1-O-O-R2 wherein
10 R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

In still another aspect, the present invention concerns a battery or a supercapacitor comprising an electrolyte composition comprising at least one compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

In a further aspect the present invention concerns a process for the manufacture of a
15 compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl using the appropriate R1-OH and the appropriate R2-OF.

In another aspect the present invention concerns a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1=R2 and R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl using the appropriate R1-OH in the presence of
20 ClF₃.

In another aspect the present invention concerns a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 is CF₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl using R2-OF in the presence of CF₂O and, optionally a
25 catalyst.

Detailed description

In the context of the present invention, the term “comprising” is intended to include the meaning of “consisting of”. In the present disclosure, designations in singular are intended to include the plural. The expression “comprised between...and...” should be understood as
30 including the limits.

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In the present disclosure “alkyl” refers to a linear or branched saturated hydrocarbon, having preferably from 1 to 5 carbon atoms. Preferred examples of alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl and tert-butyl.

The term “perfluorinated alkyl” refers to a linear or branched saturated hydrocarbon, having preferably from 1 to 5 carbon atoms wherein all the hydrogen atoms have been replaced by fluorine. Preferred examples are CF_3 , CF_3CF_2 , $\text{CF}_3\text{CF}_2\text{CF}_2$, $(\text{CF}_3)_2\text{CF}$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2$, $\text{CF}_3\text{CF}_2(\text{CF}_3)\text{CF}_2$, $(\text{CF}_3)_3\text{C}$.

The term “partially fluorinated alkyl” refers to a linear or branched saturated hydrocarbon, having preferably from 1 to 5 carbon atoms wherein at least one hydrogen atoms has been replaced by fluorine. Preferred examples are CH_2F , CHF_2 , CF_3CH_2 , CF_3CHF , $\text{CF}_3\text{CH}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2$, $(\text{CF}_3)_2\text{CH}$.

The term “normal temperature and pressure” should be understood as a temperature of around 20-25°C, preferably at 20°C; and at a pressure of 1 bar.

A first aspect of the present invention concerns a compound of formula R1-O-O-R2 (Formula (I)) wherein R1 is $\text{C}(\text{CF}_3)_3$ and R2 is a perfluorinated or partially fluorinated linear or branched alkyl and wherein R2 is different from R1.

Preferably R2 is selected from the group consisting of perfluorinated or partially fluorinated methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, and t-butyl. Preferably R2 is selected from CF_3 , CF_2CF_3 , $\text{CF}(\text{CF}_3)_2$.

In another aspect R2 is selected from CHF_2 , CF_3CHF , $\text{CF}_3\text{CF}_2\text{CHF}$, $(\text{CF}_3)_2\text{CH}$, $(\text{CF}_3)_2(\text{CH}_3)\text{C}$, $(\text{CF}_3)(\text{CH}_3)_2\text{C}$.

According to an advantageous aspect of the invention, the compound of formula (I) R1-O-O-R2 is liquid at normal temperature and pressure. Accordingly the compound of formula (I) R1-O-O-R2 may have a boiling point equal to or higher than 25°C, preferably equal to or higher than 40°C, more preferably equal to or higher than 50°C, and still more preferably equal to or higher than 70°C. The compound of formula (I) R1-O-O-R2 may have a boiling point equal to or less than 200°C, preferably equal to or less than 190°C, more preferably equal to or less than 185°C.

Advantageously, one subject-matter of the present invention is a compound selected from the groups consisting of $(\text{CF}_3)_3\text{C-O-O-CF}_3$, $(\text{CF}_3)_3\text{C-O-O-CF}_2\text{CF}_3$, $(\text{CF}_3)_3\text{C-O-O-}$

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CF(CF₃)₂, (CF₃)₃C-O-O-CHF₂, (CF₃)₃C-O-O-CHF(CF₃), (CF₃)₃C-O-O-CHF(CF₂CF₃), (CF₃)₃C-O-O-CH(CF₃)₂ and mixtures thereof.

According to a preferred embodiment, the compound of formula (I) R1-O-O-R2 for use according to the invention may have R1 is C(CF₃)₃. Therefore, the present invention concerns the use of at least one compound of formula (I) R1-O-O-R2 as electrolyte component, wherein R1 is C(CF₃)₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl.

Preferably R2 can be selected from the group consisting of perfluorinated or partially fluorinated methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, and tert-butyl. According to one aspect of the invention, R1 and R2 may be the same. According to another aspect, R1 and R2 may be different. R2 can independently be selected from the group consisting of CF₃, CF₂CF₃, CF(CF₃)₂ and C(CF₃)₃. In another aspect, R2 can independently be selected from the group consisting of CHF₂, CF₃CHF, CF₃CF₂CHF and (CF₃)₂CH.

Advantageously, the compounds of formula (I) R1-O-O-R2 wherein R1 is C(CF₃)₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl used in the present invention as electrolyte component is liquid at normal temperature and pressure. Accordingly the compound of formula (I) R1-O-O-R2 wherein R1 is C(CF₃)₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl may have a boiling point equal to or higher than 25°C, preferably equal to or higher than 40°C, more preferably equal to or higher than 50°C, and still more preferably equal to or higher than 70°C. Said compounds of formula (I) R1-O-O-R2 wherein R1 is C(CF₃)₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl may have a boiling point equal to or less than 200°C, preferably equal to or less than 190°C, more preferably equal to or less than 185°C.

Specifically, one subject-matter of the present invention is the use of at least one compound selected from the group consisting of (CF₃)₃C-O-O-C(CF₃)₃, CF₃-O-O-C(CF₃)₃, CF₃CF₂-O-O-C(CF₃)₃, CF(CF₃)₂-O-O-C(CF₃)₃, (CF₃)₃C-O-O-CHF₂, (CF₃)₃C-O-O-CHF(CF₃), (CF₃)₃C-O-O-CHF(CF₂CF₃), (CF₃)₃C-O-O-CH(CF₃)₂ and mixture thereof, as electrolyte component.

In another embodiment the present invention concerns the use of at least one compound of formula (I) R1-O-O-R2 as electrolyte component, wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

Preferably R1 and R2 can independently be selected from the group consisting of perfluorinated or partially fluorinated methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, and tert-butyl. According to one aspect of the invention, R1 and R2 may be the same. According to another aspect, R1 and R2 may be different. R1 and R2 can independently be selected from the group consisting of CF₃, CF₂CF₃, CF(CF₃)₂ and C(CF₃)₃. In another aspect, R1 and R2 can independently be selected from the group consisting of CHF₂, CF₃CHF, CF₃CF₂CHF and (CF₃)₂CH.

Advantageously the compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl used in the present invention as electrolyte component is liquid at normal temperature and pressure. Accordingly the compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may have a boiling point equal to or higher than 25°C, preferably equal to or higher than 40°C, more preferably equal to or higher than 50°C, and still more preferably equal to or higher than 70°C. Said compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may have a boiling point equal to or less than 200°C, preferably equal to or less than 190°C, more preferably equal to or less than 185°C.

Specifically one subject-matter of the present invention is the use of at least one compound selected from the group consisting of CF₃CF₂-O-O-CF₂CF₃, (CF₃)₂CF-O-O-CF(CF₃)₂, (CF₃)₃C-O-O-C(CF₃)₃, CF₃-O-O-C(CF₃)₃, CF₃CF₂-O-O-C(CF₃)₃, CF₃CF₂-O-O-CF(CF₃)₂, CF(CF₃)₂-O-O-C(CF₃)₃, (CF₃)₃C-O-O-CHF₂, (CF₃)₃C-O-O-CHFCF₃, (CF₃)₃C-O-O-CHFCF₂CF₃, (CF₃)₃C-O-O-CH(CF₃)₂ and mixtures thereof, as electrolyte component.

Preferably the compounds used in the present invention are used as electrolyte component in an electrochemical device, and more particularly in electronic displays or in energy storing and releasing devices. The compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may be used as electrolyte component in one of the following electrochemical devices:

- Electrochromic device: car or house windows, visors, eyeglasses,

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- Electrochromic flat screens: televisions, tablets, smartphones, connected devices,
- Secondary lithium batteries, lithium-sulfur batteries, lithium-air batteries, sodium batteries,
- High voltage batteries,
- 5 - Supercapacitors, in particular double-layer supercapacitors using an electrolyte,
- Energy generator, such as solar panels or organic type (OPV).

Preferably the electrochemical device may be a lithium-ion battery, a lithium-sulfur battery or a supercapacitor.

The compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or
10 partially fluorinated linear or branched alkyl may be used as additive in an electrolyte composition. Alternatively, the compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may be used as solvent or co-solvent in an electrolyte composition. Preferably the compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may be
15 used as additive, solvent or co-solvent for lithium-ion batteries, lithium-sulfur batteries or supercapacitors.

In another embodiment, the present invention concerns an electrolyte composition for an electrochemical device comprising at least one compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

20 The compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl are advantageously used in electrolyte compositions together with at least one suitable solvent known to the person skilled in the art of lithium-ion batteries, lithium-sulfur batteries or supercapacitors. For example, organic carbonates, but also lactones, formamides, pyrrolidinones, oxazolidinones, nitroalkanes, N,N-
25 substituted urethanes, sulfolanes, dialkyl sulfoxides, dialkyl sulfites, acetates, nitriles, acetamides, glycol ethers, dioxolanes, dialkyloxyethanes, trifluoroacetamides are very suitable as solvents.

Preferably the electrolyte composition of the present invention comprises at least one solvent, preferably a cyclic or non-cyclic carbonate, more preferably selected from ethylene
30 carbonate, dimethyl carbonate, triglyme or mixture thereof.

The compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may advantageously be used as a solvent, a co-solvent, or an additive in a concentration equal to or more than 1% by weight, preferably equal to or more than 3% by weight, more preferably equal to or more than 4% by weight, most preferably around 5% by weight relative to the total weight of the electrolyte composition. The compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl may advantageously be used as a solvent, a co-solvent, or an additive in a concentration equal to or less than 20% by weight, preferably equal to or less than 10% by weight, more preferably equal to or less than 6% by weight relative to the total weight of the electrolyte composition.

Accordingly another aspect of the present invention concerns the use of a compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl in an electrolyte composition wherein the concentration of said compound is equal to or more than 1% by weight, preferably equal to or more than 3% by weight, more preferably equal to or more than 4% by weight, most preferably around 5% by weight relative to the total weight of the electrolyte composition. Another aspect of the present invention concerns the use of a compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl in an electrolyte composition wherein the concentration of said compound is equal to or less than 20% by weight, preferably equal to or less than 10% by weight, more preferably equal to or less than 6% by weight relative to the total weight of the electrolyte composition.

In another aspect, the compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl are advantageously used in electrolyte compositions together with at least one electrolyte salt known to the person skilled in the art of lithium-ion batteries, lithium-sulfur batteries or supercapacitors. Such salts have the general formula M_aA_b , wherein M represents a metal cation, A represents an anion, a represents 1, 2, 3 or 4, b represents 1, 2, 3 or 4, and the overall charge of the salt M_aA_b is 0. M is preferably selected from Li^+ and NR_4^+ . Preferred anions are PF_6^- , $PO_2F_2^-$, AsF_6^- , BF_4^- , ClO_4^- , $N(CF_3SO_2)^{2-}$, $N(FSO_2)^{2-}$ and $N(i-C_3F_7SO_2)^{2-}$. Preferably the electrolyte composition of the present invention comprises at least one lithium salt, preferably selected from LiTFSI or LiPF₆. The concentration of the electrolyte salt is preferably between 0.8 and 1.2 molar, more

preferably 1.0 molar. The compound of formula (I) wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl can be introduced into the electrolyte composition separately or in the form of a mixture with other compounds, for example as a mixture with one or more solvents used in the electrolyte composition or together with the electrolyte salt or together with other additives.

Advantageously the compounds of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl display a good compatibility with an electrolyte composition.

In another embodiment, the present invention concerns a battery, preferably a high-voltage battery, or a supercapacitor comprising an electrolyte composition comprising at least one compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl. Batteries according to the invention may be low temperature batteries (working typically between -40°C and 0°C), or batteries working higher temperatures, between 0° and the ambient temperature, or at a temperature equal to or higher than 25°C, preferably equal to or higher than 40°C, more preferably equal to or higher than 50°C, and still more preferably equal to or higher than 70°C.

Lithium-ion batteries comprise an anode, preferably an anode made from carbon on a copper foil, a cathode, preferably a cathode made from lithium metal oxides on an aluminium foil, a separator, preferably a separator made from an insulating polymer, and a solvent composition or an electrolyte composition as described above. The foils used for anode and cathode are also called current collectors.

In another aspect, the present invention relates to a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl using either the appropriate R1OH and the appropriate R2OF or the appropriate R2OH and the appropriate R1OF. Said process may comprise the step consisting of reacting either a compound of formula R1OH and a compound of formula R2OF or a compound of formula R2OH and a compound of formula R1OF together to obtain a compound of formula (I) R1-O-O-R2, wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

In an aspect of this embodiment R1 and R2 may be the same. In another aspect R1 and R2 may be different.

The reaction of this embodiment can be carried out in a static or continuous-flow reactor.

5 The reaction of this embodiment may be carried out at a temperature equal to or more than -196°C , preferably equal to or more than -100°C , more preferably equal to or more than -78°C . The reaction of this embodiment may be carried out at a temperature equal to or less than 180°C , preferably equal to or less than 100°C , more preferably equal to or less than 50°C . Specifically the reaction of this embodiment may be carried out at a temperature of about 0°C .

10 In another aspect, the present invention relates to a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 is $\text{C}(\text{CF}_3)_3$ and R2 is perfluorinated or partially fluorinated linear or branched alkyl using either the appropriate R1OH and the appropriate R2OF or the appropriate R2OH and the appropriate R1OF. Said process may
15 comprise the step consisting of reacting either a compound of formula R1OH and a compound of formula R2OF or a compound of formula R2OH and a compound of formula R1OF together to obtain a compound of formula (I) R1-O-O-R2 , wherein R1 is $\text{C}(\text{CF}_3)_3$ and R2 is perfluorinated or partially fluorinated linear or branched alkyl.

20 In an aspect of this embodiment R1 and R2 may be the same. In another aspect R1 and R2 may be different.

The reaction of this embodiment can be carried out in a static or continuous-flow reactor.

25 The reaction of this embodiment may be carried out at a temperature equal to or more than -196°C , preferably equal to or more than -100°C , more preferably equal to or more than -78°C . The reaction of this embodiment may be carried out at a temperature equal to or less than 180°C , preferably equal to or less than 100°C , more preferably equal to or less than 50°C . Specifically the reaction of this embodiment may be carried out at a temperature of about 0°C .

30 In another aspect, the present invention relates to a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl having wherein $\text{R1} = \text{R2}$ using R1OH in the presence of

ClF₃ as described in GB1301148. The synthesis of perfluoro-tert-butyl peroxide by oxidation of perfluoro-tert-butyl alcohol with chlorine tetrafluoride is further exemplified in the scientific publications "Bis(perfluoro-t-butyl)peroxide" of Gould et al (Chemical Communications, 1970) and in "Organic compounds bearing a difluoroaminooxy group" of Fokin et al (Russian Chemical Bulletin, Vol. 48, No.1, January 1999).

Preferably the reaction may be performed using 2 equivalents of R1OH.

Preferably R1 and R2 are different from CF₃ or (CF₃)₃.

The reaction of this embodiment can be carried out in a static or continuous-flow reactor.

The reaction of this embodiment may be carried out at a temperature equal to or more than -196°C, preferably equal to or more than -100°C, more preferably equal to or more than -78°C. The reaction of this embodiment may be carried out at a temperature equal to or less than 30°C, preferably equal to or less than 15°C, more preferably equal to or less than 0°C. Specifically the reaction of this embodiment may be carried out at a temperature of -78°C.

In another aspect, the present invention relates to a process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 is CF₃ and R2 is perfluorinated or partially fluorinated linear or branched alkyl using the appropriate hypofluorite R2OF in the presence of CF₂O as described in EP3078657 and in US 2007/0049774. The synthesis of perfluorodimethyl peroxide by reaction between COF₂ and trifluoromethyl hypofluorite CF₃OF is further exemplified in US 3,230,264.

In one alternative the carbonyl fluoride is prepared in situ in a flow reactor, preferably prepared in situ from F₂ and CO. The mixture of F₂ and CO is suitably ignited to prepare COF₂, for example by means of an electric spark.

Preferably R2 is different from R1.

Optionally the reaction is carried out in the presence of a catalyst. Preferably the catalyst is selected from the group consisting of AgF, CuF, CuF₂, BaF₂, CsF, NiF₂, preferably AgF.

The reaction of this embodiment can be carried out in a static or continuous-flow reactor. Preferably, the reactor is made of a material suitable for reactions involving molecular

fluorine, for example made of Monel® 400 or nickel. Also preferably, the reaction is carried out in a continuous-flow reactor.

The reaction of this embodiment may be carried out at a temperature equal to or more than -20°C , preferably equal to or more than 0°C , more preferably equal to or more than 20°C .

- 5 The reaction of this embodiment may be carried out at a temperature equal to or less than 180°C , preferably equal to or less than 140°C , more preferably equal to or less than 50°C . Specifically the reaction of this embodiment may be carried out at a temperature of 25°C .

Should the disclosure of any patents, patent applications and publications, which are
10 incorporated herein by reference, conflicts with the description of the present invention to the extent that it may render a term unclear, the present description shall take precedence.

The invention will now be further described in examples, which are given by way of illustration and which are no intended to limit the specification or the claims in any manner.

15 **Examples**

Example 1: Manufacture of $(\text{CF}_3)_3\text{COOCF}_3$

An equimolar mixture of carbonyl fluoride (COF_2) and perfluoro-t-butyl hypofluorite ($(\text{CF}_3)_3\text{COF}$) is allowed to react in a static reactor made from Monel 400 in the presence of
20 silver fluoride AgF at 25°C for 24 hours.

Example 2: Manufacture of $\text{CF}_3\text{CF}_2\text{OOCF}_2\text{CF}_3$

An equimolar mixture of perfluoro-ethanol ($\text{CF}_3\text{CF}_2\text{OH}$) and chlorine trifluoride (ClF_3) is allowed to react in a static reactor at -78°C for 12 hours.

25

Example 3: Manufacture of $(\text{CF}_3)_3\text{COOCF}_2\text{CF}_3$

An equimolar mixture of perfluoro-t-butyl hypofluorite ($(\text{CF}_3)_3\text{COF}$) and perfluoro-ethanol ($\text{CF}_3\text{CF}_2\text{OH}$) is allowed to react in a static reactor at 0°C for 12 hours.

30 Example 4: Preparation of electrolyte compositions

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Battery grade 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (1/2, v/v) is used as the base electrolyte solution under dry room atmosphere. The following electrolyte compositions were used:

Example A (comparative): No additive

5 Example B (Invention): 0.1% (CF₃)₃COOC(CF₃)₃

Example C (Invention): 0.5% (CF₃)₃COOC(CF₃)₃

It appears that the perfluoroperoxide (CF₃)₃COOC(CF₃)₃ displays good compatibility with the electrolyte composition at various temperature and pressure.

CLAIMS

1. Compound of formula R1-O-O-R2 (Formula (I)) wherein R1 is C(CF₃)₃ and R2 is a perfluorinated or partially fluorinated linear or branched alkyl and wherein R2 is different
5 from R1.

2. Compound according to claim 1, wherein said compound is liquid at normal temperature and pressure.

3. Compound according to any one of claims 1 or 2, wherein said compound of formula (I) has a boiling point equal to or higher than 25°C, preferably equal to or higher than
10 40°C, more preferably equal to or higher than 50°C and still more preferably equal to or higher than 70°C.

4. Compound according to any one of claims 1 to 3, wherein said compound is selected from the groups consisting of (CF₃)₃C-O-O-CF₃, (CF₃)₃C-O-O-CF₂CF₃, (CF₃)₃C-O-O-CF(CF₃)₂, (CF₃)₃C-O-O-CHF₂, (CF₃)₃C-O-O-CHF₂CF₃, (CF₃)₃C-O-O-CHF₂CF₂CF₃, (CF₃)₃C-O-O-CH(CF₃)₂ and mixtures thereof.
15

5. Use of at least one compound of formula (I) R1-O-O-R2 as electrolyte component wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl.

6. Use of at least one compound of formula (I) according to claim 5, wherein said compound of formula (I) is liquid at normal temperature and pressure.

7. Use of at least one compound of formula (I) according to any one of claims 5 to 6, wherein said compound of formula (I) has a boiling point equal to or higher than 25°C, preferably equal to or higher than 40°C, more preferably equal to or higher than 50°C and still more preferably equal to or higher than 70°C.
20

8. Use of at least one compound of formula (I) according to any one of claims 5 to 7, said compound is selected from the group consisting of (CF₃)₃C-O-O-C(CF₃)₃, CF₃-O-O-C(CF₃)₃, CF₃CF₂-O-O-C(CF₃)₃, CF(CF₃)₂-O-O-C(CF₃)₃, (CF₃)₃C-O-O-CHF₂, (CF₃)₃C-O-O-CHF₂CF₃, (CF₃)₃C-O-O-CHF₂CF₂CF₃, (CF₃)₃C-O-O-CH(CF₃)₂ and mixtures thereof.
25

9. Use of at least one compound of formula (I) according to any one of claims 5 to 8 as additive in an electrolyte composition, or as a solvent or a co-solvent in an electrolyte composition.

10. An electrolyte composition for an electrochemical device comprising at least one compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl, preferably selected from a lithium-ion battery, lithium-sulfur battery or supercapacitor.

11. A battery or a supercapacitor comprising an electrolyte composition as defined in claim 10.

12. Process for the manufacture of a compound of formula R1-O-O-R2 according to any one of claims 1 to 4, using the appropriate hypofluorite R2OF in the presence of CF₂O and optionally a catalyst.

13. Process according to claim 12, wherein the catalyst is selected from the group consisting of AgF, CuF, CuF₂, BaF₂, CsF, NiF₂, preferably AgF.

14. Process for the manufacture of a compound of formula (I) R1-O-O-R2 wherein R1 and R2 are perfluorinated or partially fluorinated linear or branched alkyl using the appropriate R1OH and the appropriate R2OF.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/075791

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C409/16 H01M10/0569
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)
C07C 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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 301 148 A (ALLIED CHEMICAL) 29 December 1972 (1972-12-29) cited in the application page 2, lines 53-61; claim 1; examples 1, 2A	1-14
A	----- F HOHORST ET AL: "Direct synthesis of fluorocarbon peroxides?II The addition of fluoroperoxytrifluoromethane to alkenes", JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY, vol. 28, no. supplement 1, 1976, pages 63-66, XP055214103, ISSN: 0022-1902, DOI: 10.1016/0022-1902(76)80597-0 table 1; compounds IV-IX ----- -/-	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

6 March 2018

Date of mailing of the international search report

21/03/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/075791

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/049774 A1 (R.G. SYVRET, ET AL.) 1 March 2007 (2007-03-01) examples 1-3 -----	1-4,12, 13
A	US 2016/118690 A1 (M. BOMKAMP, ET AL.) 28 April 2016 (2016-04-28) claim 1; example 2 -----	1-11
A	WO 2014/016271 A1 (SOLVAY) 30 January 2014 (2014-01-30) claims 1-6 -----	1-11
A	WO 2013/174697 A1 (SOLVAY) 28 November 2013 (2013-11-28) claim 1 -----	1-11
X,P	EP 3 078 657 A1 (SOLVAY) 12 October 2016 (2016-10-12) cited in the application example 1c -----	12,13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2017/075791

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

Perfluorinated and partially fluorinated dialkyl peroxides
as electrolyte components

2. claim: 14

Manufacture of perfluorinated and partially fluorinated
dialkyl peroxides

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/075791

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			WO	2013174697 A1		28-11-2013

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