



(51) International Patent Classification:

H01M 10/0569 (2010.01) *H01M 10/0525* (2010.01)
H01M 10/052 (2010.01) *H01M 4/485* (2010.01)
H01M 6/16 (2006.01) *H01M 4/505* (2010.01)
H01M 10/0568 (2010.01) *H01M 4/587* (2010.01)
H01M 10/0567 (2010.01)

(21) International Application Number:

PCT/US2013/029825

(22) International Filing Date:

8 March 2013 (08.03.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/654,190 1 June 2012 (01.06.2012) US

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FLUORINATED ELECTROLYTE COMPOSITIONS

(57) Abstract: Electrolyte compositions comprising novel fluorine- containing carboxylic acid ester solvents are described. The fluorine-containing carboxylic acid ester solvents are represented by the formula $R^1-C(=O)-R^2$, wherein R^1 is CH_3CH_2- and R^2 is $-CH_2CHF_2$, R^1 is CH_3- and R^2 is $-CH^2CH_2CHF_2$, R^1 is CH_3CH_2- and R^2 is $-CH^2CH_2CHF_2$, R^1 is $CHF_2CH_2CH_2-$ and R^2 is $-CH_2CH_3$, or R^1 is CHF_2CH_2- and R^2 is $-CH_2CH_3$. The electrolyte compositions are useful in electrochemical cells, such as lithium ion batteries.



TITLE

FLUORINATED ELECTROLYTE COMPOSITIONS

5 This application claims priority under 35 U.S.C. §119(e) from, and claims the benefit of, U.S. Provisional Application No. 61/654,190 filed June 1, 2012, which is by this reference incorporated in its entirety as a part hereof for all purposes.

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Technical Field

 The disclosure hereof relates to electrolyte compositions containing novel fluorine-containing
15 carboxylic acid ester solvents, which are useful in electrochemical cells, such as lithium ion batteries.

Background

20 Carbonate compounds are currently used as electrolyte solvents for non-aqueous batteries containing electrodes made from alkali metals, alkaline earth metals, or compounds comprising these metals, for example lithium ion batteries. Current lithium ion battery electrolyte
25 solvents typically contain one or more linear carbonates, such as ethyl methyl carbonate, dimethyl carbonate, or diethylcarbonate; and a cyclic carbonate, such as ethylene carbonate. However, at battery voltages above 4.4 V these electrolyte solvents can decompose, which can result
30 in a loss of battery performance. Additionally, there are safety concerns with the use of these electrolyte

solvents because of their low boiling point and high flammability.

To overcome the limitations of commonly used non-
5 aqueous electrolyte solvents, various fluorine-containing
carboxylic acid ester electrolyte solvents have been
investigated for use in lithium ion batteries (see, for
example, Nakamura *et al* in JP 4/328,915-B2, JP 3/444,607-
B2, and U.S. Patent No. 8,097,368). Although these
10 fluorine-containing carboxylic acid ester electrolyte
solvents can be used in lithium ion batteries having high
voltage cathodes, such the 4 V spinel LiMn_2O_4 cathode,
cycling performance can be limited, particularly at high
temperatures.

15

Despite the efforts in the art as described above, a
need remains for electrolyte solvents, and compositions
thereof, that will have improved cycling performance at
high temperature when used in a lithium ion battery,
20 particularly such a battery that operates at high voltage
(*i.e.* up to about 5 V).

Summary

25 In one embodiment, there is provided herein an
electrolyte composition comprising (a) at least one
electrolyte salt, and (b) at least one fluorine-containing
carboxylic acid ester represented by the formula $\text{R}^1\text{-C(O)O-}$
 R^2 , wherein

30 R^1 is $\text{CH}_3\text{CH}_2\text{-}$ and R^2 is $\text{-CH}_2\text{CHF}_2$,

R^1 is CH_3- and R^2 is $-\text{CH}_2\text{CH}_2\text{CHF}_2$,
 R^1 is CH_3CH_2- and R^2 is $-\text{CH}_2\text{CH}_2\text{CHF}_2$,
 R^1 is $\text{CHF}_2\text{CH}_2\text{CH}_2-$ and R^2 is $-\text{CH}_2\text{CH}_3$, or
 R^1 is CHF_2CH_2- and R^2 is $-\text{CH}_2\text{CH}_3$.

5

In another embodiment of the subject matter hereof, there is provided an electrochemical cell comprising:

(a) a housing;

(b) an anode and a cathode disposed in said housing
 10 and in ionically conductive contact with one another;

(c) an electrolyte composition disposed in said housing and providing an ionically conductive pathway between said anode and said cathode, wherein the electrolyte composition comprises:

15 (i) at least one electrolyte salt; and
 (ii) at least one fluorine-containing carboxylic acid ester represented by the formula $R^1-\text{C}(\text{O})\text{O}-R^2$,
 wherein

R^1 is CH_3CH_2- and R^2 is $-\text{CH}_2\text{CHF}_2$,

20 R^1 is CH_3- and R^2 is $-\text{CH}_2\text{CH}_2\text{CHF}_2$,

R^1 is CH_3CH_2- and R^2 is $-\text{CH}_2\text{CH}_2\text{CHF}_2$,

R^1 is $\text{CHF}_2\text{CH}_2\text{CH}_2-$ and R^2 is $-\text{CH}_2\text{CH}_3$, or

R^1 is CHF_2CH_2- and R^2 is $-\text{CH}_2\text{CH}_3$; and

(d) a porous separator between said anode and said
 25 cathode.

Detailed Description

As used above and throughout the description of the
 30 invention, the following terms, unless otherwise

indicated, shall be defined as follows:

The term "electrolyte composition" as used herein, refers to a chemical composition suitable for use as an electrolyte in an electrochemical cell. An electrolyte composition typically comprises at least one solvent and at least one electrolyte salt.

The term "electrolyte salt" as used herein, refers to an ionic salt that is at least partially soluble in the solvent of the electrolyte composition and that at least partially dissociates into ions in the solvent of the electrolyte composition to form a conductive electrolyte composition.

15

The term "anode" refers to the electrode of an electrochemical cell, at which oxidation occurs. In a galvanic cell, such as a battery, the anode is the negatively charged electrode. In a secondary (i.e. rechargeable) battery, the anode is the electrode at which oxidation occurs during discharge and reduction occurs during charging.

The term "cathode" refers to the electrode of an electrochemical cell, at which reduction occurs. In a galvanic cell, such as a battery, the cathode is the positively charged electrode. In a secondary (i.e. rechargeable) battery, the cathode is the electrode at which reduction occurs during discharge and oxidation occurs during charging.

30

The term "lithium ion battery" refers to a type of rechargeable battery in which lithium ions move from the anode to the cathode during discharge, and from the cathode to the anode during charge.

Disclosed herein are electrolyte compositions comprising novel fluorine-containing carboxylic acid esters. The electrolyte compositions are useful in electrochemical cells, particularly lithium ion batteries. Specifically, the electrolyte compositions disclosed herein comprise at least one fluorine-containing carboxylic acid ester represented by the formula $R^1-C(O)O-R^2$, wherein

- R^1 is CH_3CH_2- and R^2 is $-CH_2CHF_2$,
- R^1 is CH_3- and R^2 is $-CH_2CH_2CHF_2$,
- R^1 is CH_3CH_2- and R^2 is $-CH_2CH_2CHF_2$,
- R^1 is $CHF_2CH_2CH_2-$ and R^2 is $-CH_2CH_3$, or
- R^1 is CHF_2CH_2- and R^2 is $-CH_2CH_3$.

In one embodiment, the fluorine-containing carboxylic acid ester is $CH_3CH_2-C(O)O-CH_2CHF_2$ (2,2-difluoroethyl propionate). In another embodiment, the fluorine-containing carboxylic acid ester is $CH_3-C(O)O-CH_2CH_2CHF_2$ (3,3-difluoropropyl acetate).

The fluorine-containing carboxylic acid esters disclosed herein can be prepared using methods known in the art. For example, acetyl chloride may be reacted with 2,2-difluoroethanol (with or without a basic catalyst) to form 2,2-difluoroethyl acetate.

Additionally, 2,2-difluoroethyl acetate and 2,2-difluoroethyl propionate may be prepared using the method described by Wiesenhofer *et al* (WO 2009/040367 A1, Example 5). Alternatively, 2,2-difluoroethyl acetate and 2,2-difluoroethyl propionate can be prepared using the method described in the examples herein below. Other fluorine-containing carboxylic acid esters may be prepared using the same method using different starting carboxylate salts. It is desirable to purify the fluorine-containing carboxylic acid esters to a purity level of at least about 99.9%, more particularly at least about 99.99%. These fluorinated esters may be purified using distillation methods such as vacuum distillation or spinning band distillation.

15

The electrolyte compositions disclosed herein also contain at least one electrolyte salt. Suitable electrolyte salts include without limitation

lithium hexafluorophosphate (LiPF_6),
lithium tris(pentafluoroethyl)trifluorophosphate
($\text{LiPF}_3(\text{C}_2\text{F}_5)_3$),
lithium bis(trifluoromethanesulfonyl)imide,
lithium bis(perfluoroethanesulfonyl)imide,
lithium (fluorosulfonyl)
(nonafluorobutanesulfonyl)imide,
lithium bis(fluorosulfonyl)imide,
lithium tetrafluoroborate,
lithium perchlorate,
lithium hexafluoroarsenate,
lithium trifluoromethanesulfonate,

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lithium tris (trifluoromethanesulfonyl)methide,
lithium bis(oxalato)borate,
lithium difluoro(oxalato)borate,
 $\text{Li}_2\text{B}_{12}\text{F}_{12-x}\text{H}_x$ where x is equal to 0 to 8, and
5 mixtures of lithium fluoride and anion receptors such
as $\text{B}(\text{OC}_6\text{F}_5)_3$.

Mixtures of two or more of these or comparable
electrolyte salts may also be used. In one embodiment,
10 the electrolyte salt is lithium hexafluorophosphate. The
electrolyte salt can be present in the electrolyte
composition in an amount of about 0.2 to about 2.0 M, more
particularly about 0.3 to about 1.5 M, and more
particularly about 0.5 to about 1.2 M.

15

The electrolyte composition disclosed herein may
further comprise at least one co-solvent. Examples of
suitable co-solvents include without limitation one or
more carbonates. Suitable carbonates include ethyl
20 methyl carbonate, dimethyl carbonate, diethyl carbonate,
ethylene carbonate, propylene carbonate, vinylethylene
carbonate, fluoroethylene carbonate, 2,2,2-trifluoroethyl
carbonate, and methyl 2,2,3,3-tetrafluoropropyl carbonate.
It is desirable to use a co-solvent that is battery grade
25 or has a purity level of at least about 99.9%, and more
particularly at least about 99.99%. In one embodiment,
the co-solvent is ethylene carbonate.

In the electrolyte compositions disclosed herein, the
30 fluorine-containing carboxylic acid esters and the co-

solvent may be combined in various ratios to form a solvent mixture, depending on the desired properties of the electrolyte composition. In one embodiment, the fluorinated carboxylic acid ester comprises about 10% to about 90% by weight of the solvent mixture. In another embodiment, the fluorinated carboxylic acid ester comprises about 40% to about 90% by weight of the solvent mixture. In another embodiment, the fluorinated carboxylic acid ester comprises about 50% to about 80% by weight of the solvent mixture. In another embodiment, the fluorinated carboxylic acid ester comprises about 60% to about 80% by weight of the solvent mixture. In another embodiment, the fluorinated carboxylic acid ester comprises about 65% to about 75% by weight of the solvent mixture. In another embodiment, the fluorinated carboxylic acid ester comprises about 70% by weight of the solvent mixture.

In another embodiment, the electrolyte composition comprises a solvent mixture containing the fluorinated carboxylic acid ester $\text{CH}_3\text{CH}_2\text{-C(O)O-CH}_2\text{CHF}_2$ and ethylene carbonate, wherein $\text{CH}_3\text{CH}_2\text{-C(O)O-CH}_2\text{CHF}_2$ comprises about 50% to about 80% by weight of the solvent mixture. In another embodiment, the nonaqueous electrolyte composition contains a solvent mixture of the fluorinated carboxylic acid ester $\text{CH}_3\text{CH}_2\text{-C(O)O-CH}_2\text{CHF}_2$ and ethylene carbonate, wherein $\text{CH}_3\text{CH}_2\text{-C(O)O-CH}_2\text{CHF}_2$ comprises about 70% by weight of the solvent mixture.

In another embodiment, the electrolyte composition

comprises a solvent mixture containing the fluorinated carboxylic acid ester $\text{CH}_3\text{-C(O)O-CH}_2\text{CH}_2\text{CHF}_2$ and ethylene carbonate, wherein $\text{CH}_3\text{-C(O)O-CH}_2\text{CH}_2\text{CHF}_2$ comprises about 50% to about 80% by weight of the solvent mixture. In

5 another embodiment, the nonaqueous electrolyte composition contains a solvent mixture of the fluorinated carboxylic acid ester $\text{CH}_3\text{-C(O)O-CH}_2\text{CH}_2\text{CHF}_2$ and ethylene carbonate, wherein $\text{CH}_3\text{-C(O)O-CH}_2\text{CH}_2\text{CHF}_2$ comprises about 70% by weight of the solvent mixture.

10

The electrolyte composition disclosed herein may also contain at least one film-forming additive. Suitable film-forming additives include without limitation

15 fluoroethylene carbonate (also referred to herein as 4-fluoro-1,3-dioxolan-2-one, CAS No. 114435-02-8) and its derivatives,

ethylene sulfate and its derivatives,
vinyl ethylene carbonate and its derivatives,
vinylene carbonate and its derivatives,
20 maleic anhydride and its derivatives, and
vinyl acetate.

In one embodiment, the film-forming additive is fluoroethylene carbonate.

25 The film-forming additive, if used, is generally present in an amount of about 0.01% to about 5%, more particularly about 0.1% to about 2%, and more particularly about 0.5% to about 1.5% by weight of the total electrolyte composition. It is desirable to purify these
30 film-forming additives to a purity level of at least about

99.0%, more particularly at least about 99.9%.

Purification may be done using known methods, as described above. These additives are available commercially; fluoroethylene carbonate, for example, is available from
5 companies such as China LangChem INC. (Shanghai, China) and MTI Corp. (Richmond, CA).

In another embodiment, the invention provides an electrochemical cell comprising a housing, an anode and a
10 cathode disposed in the housing and in ionically conductive contact with one another, an electrolyte composition, as described above, providing an ionically conductive pathway between the anode and the cathode, and a porous or microporous separator between the anode and
15 the cathode. The housing may be any suitable container to house the electrochemical cell components. The anode and the cathode may be comprised of any suitable conducting material depending on the type of electrochemical cell. Suitable examples of anode
20 materials include without limitation lithium metal, lithium metal alloys, lithium titanate, aluminum, platinum, palladium, graphite, transition metal oxides, and lithiated tin oxide. Suitable examples of cathode materials include without limitation graphite, aluminum,
25 platinum, palladium, electroactive transition metal oxides comprising lithium or sodium, indium tin oxide, and conducting polymers such as polypyrrole and polyvinylferrocene.

30 The porous separator serves to prevent short

circuiting between the anode and the cathode. The porous separator typically consists of a single-ply or multi-ply sheet of a microporous polymer such as polyethylene, polypropylene, or a combination thereof. The pore size of the porous separator is sufficiently large to permit transport of ions, but small enough to prevent contact of the anode and cathode either directly or from particle penetration or dendrites which can form on the anode and cathode.

10

In another embodiment, the electrochemical cell is a lithium ion battery. Suitable cathode materials for a lithium ion battery include without limitation electroactive transition metal oxides comprising lithium, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , or LiV_3O_8 ; oxides of layered structure such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ where $x+y+z$ is about 1, $\text{LiCo}_{0.2}\text{Ni}_{0.2}\text{O}_2$, LiFePO_4 , LiMnPO_4 , LiCoPO_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiVPO_4F ; mixed metal oxides of cobalt, manganese, and nickel such as those described in U.S. Patent No. 6,964,828 (Lu) and U.S. Patent No. 7,078,128 (Lu); nanocomposite cathode compositions such as those described in U.S. Patent No. 6,680,145 (Obrovac); lithium-rich layered-layered composite cathodes such as those described in U.S. Patent No. 7,468,223; and cathodes such as those described in U.S. Patent No. 7,718,319 and the references therein.

In another embodiment, the cathode in the lithium ion battery hereof comprises a cathode active material exhibiting greater than 30 mAh/g capacity in the potential

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range greater than 4.6 V versus a Li/Li⁺ reference electrode. One example of such a cathode is a stabilized manganese cathode comprising a lithium-containing manganese composite oxide having a spinel structure as cathode active material. The lithium-containing manganese composite oxide in a cathode suitable for use herein comprises oxides of the formula $\text{Li}_x\text{Ni}_y\text{M}_z\text{Mn}_{2-y-z}\text{O}_{4-d}$, wherein x is 0.03 to 1.0; x changes in accordance with release and uptake of lithium ions and electrons during charge and discharge; y is 0.3 to 0.6; M comprises one or more of Cr, Fe, Co, Li, Al, Ga, Nb, Mo, Ti, Zr, Mg, Zn, V, and Cu; z is 0.01 to 0.18; and d is 0 to 0.3. In one embodiment in the above formula, y is 0.38 to 0.48, z is 0.03 to 0.12, and d is 0 to 0.1. In one embodiment in the above formula, M is one or more of Li, Cr, Fe, Co and Ga. Stabilized manganese cathodes may also comprise spinel-layered composites which contain a manganese-containing spinel component and a lithium rich layered structure, as described in U.S. Patent No. 7,303,840.

20

A cathode active material suitable for use herein can be prepared using methods such as the hydroxide precursor method described by Liu *et al* (*J. Phys. Chem. C* 13:15073-15079, 2009). In that method, hydroxide precursors are precipitated from a solution containing the required amounts of manganese, nickel and other desired metal(s) acetates by the addition of KOH. The resulting precipitate is oven-dried and then fired with the required amount of LiOH•H₂O at about 800 to about 950°C in oxygen for 3 to 24 hours, as described in detail in the examples

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herein. Alternatively, the cathode active material can be prepared using a solid phase reaction process or a sol-gel process as described in U.S. Patent No. 5,738,957 (Amine).

5

A cathode, in which the cathode active material is contained, suitable for use herein may be prepared by methods such as mixing an effective amount of the cathode active material (e.g. about 70 wt% to about 97 wt%), a polymer binder, such as polyvinylidene difluoride, and conductive carbon in a suitable solvent, such as N-methylpyrrolidone, to generate a paste, which is then coated onto a current collector such as aluminum foil, and dried to form the cathode.

15

A lithium ion battery as disclosed herein can further contain an anode, which comprises an anode active material that is capable of storing and releasing lithium ions. Examples of suitable anode active materials include without limitation lithium alloys such as lithium-aluminum alloy, lithium-lead alloy, lithium-silicon alloy, lithium-tin alloy and the like; carbon materials such as graphite and mesocarbon microbeads (MCMB); phosphorus-containing materials such as black phosphorus, MnP_4 and CoP_3 ; metal oxides such as SnO_2 , SnO and TiO_2 ; and lithium titanates such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 . In one embodiment, the anode active material is lithium titanate or graphite.

30

An anode can be made by a method similar to that

described above for a cathode wherein, for example, a binder such as a vinyl fluoride-based copolymer is dissolved or dispersed in an organic solvent or water, which is then mixed with the active, conductive material to obtain a paste. The paste is coated onto a metal foil, preferably aluminum or copper foil, to be used as the current collector. The paste is dried, preferably with heat, so that the active mass is bonded to the current collector. Suitable anode active materials and anodes are available commercially from companies such as Hitachi NEI Inc. (Somerset, NJ), and Farasis Energy Inc. (Hayward, CA).

A lithium ion battery as disclosed herein also contains a porous separator between the anode and cathode. The porous separator serves to prevent short circuiting between the anode and the cathode. The porous separator typically consists of a single-ply or multi-ply sheet of a microporous polymer such as polyethylene, polypropylene, polyamide or polyimide, or a combination thereof. The pore size of the porous separator is sufficiently large to permit transport of ions to provide ionically conductive contact between the anode and cathode, but small enough to prevent contact of the anode and cathode either directly or from particle penetration or dendrites which can form on the anode and cathode. Examples of porous separators suitable for use herein are disclosed in U.S. Application SN 12/963,927 (filed 09 Dec 2010, U.S. Patent Application Publication No. 2012/0149852), which is by this reference incorporated in its entirety as a part hereof for all

purposes.

The housing of the lithium ion battery hereof may be any suitable container to house the lithium ion battery components described above. Such a container may be fabricated in the shape of small or large cylinder, a prismatic case or a pouch.

The lithium ion battery hereof may be used for grid storage or as a power source in various electronically-powered or -assisted devices ("Electronic Device") such as a transportation device (including a motor vehicle, automobile, truck, bus or airplane), a computer, a telecommunications device, a camera, a radio or a power tool.

EXAMPLES

The subject matter disclosed herein is further defined in the following examples. It should be understood that these examples, while describing various features of certain particular embodiments of some of the inventions hereof, are given by way of illustration only.

The meaning of abbreviations used is as follows: "g" means gram(s), "mg" means milligram(s), "µg" means microgram(s), "L" means liter(s), "mL" means milliliter(s), "mol" means mole(s), "mmol" means millimole(s), "M" means molar concentration, "wt%" means percent by weight, "mm" means millimeter(s), "ppm" means

parts per million, "h" means hour(s), "min" means minute(s), "Hz" means hertz, "mS" means millisiemen(s), "mA" mean milliamp(s), "mAh/g" mean milliamp hour(s) per gram, "V" means volt(s),

5 "xC" refers to a constant current that can fully charge/discharge the cathode in 1/x hours, "SOC" means state of charge, "SEI" means solid electrolyte interface formed on the surface of the electrode material, "kPa" means kilopascal(s), "rpm" means revolutions per minute,

10 "psi" means pounds per square inch.

Materials and Methods:

Preparation of 2,2-Difluoroethyl Acetate

15 Potassium acetate (Aldrich, 99%) was dried at 100 °C under a vacuum of 0.5-1 mm of Hg (66.7-133 Pa) for 4 to 5 h. The dried material had a water content of less than 5 ppm, as determined by Karl Fischer titration. In a dry box, 212 g (2.16 mol, 8 mol% excess) of the dried

20 potassium acetate was placed into a 1.0-L, 3 neck round bottom flask containing a heavy magnetic stir bar. The flask was removed from the dry box, transferred into a fume hood, and equipped with a thermocouple well, a dry-ice condenser, and an addition funnel.

25

Sulfolane (500 mL, Aldrich, 99%, 600 ppm of water as determined by Karl Fischer titration) was melted and added to the 3 neck round bottom flask as a liquid under a flow of nitrogen. Agitation was started and the temperature

30 of the reaction mixture was brought to about 100°C.

HCF₂CH₂Br (290 g, 2 mol, E.I. du Pont de Nemours and Company, 99%) was placed in the addition funnel and was slowly added to the reaction mixture. The addition was mildly exothermic and the temperature of the reaction mixture rose to 120-130°C in 15-20 min after the start of the addition. The addition of HCF₂CH₂Br was kept at a rate which maintained the internal temperature at 125-135°C. The addition took about 2-3 h. The reaction mixture was agitated at 120-130°C for an additional 6 h (typically the conversion of bromide at this point was about 90-95%). Then, the reaction mixture was cooled down to room temperature and was agitated overnight. Next morning, heating was resumed for another 8 h.

At this point the starting bromide was not detectable by NMR and the crude reaction mixture contained 0.2-0.5% of 1,1-difluoroethanol. The dry-ice condenser on the reaction flask was replaced by a hose adapter with a Teflon® valve and the flask was connected to a mechanical vacuum pump through a cold trap (-78°C, dry-ice/acetone). The reaction product was transferred into the cold trap at 40-50°C under a vacuum of 1-2 mm Hg (133 to 266 Pa). The transfer took about 4-5 h and resulted in 220-240 g of crude HCF₂CH₂OC(O)CH₃ of about 98-98.5% purity, which was contaminated by a small amount of HCF₂CH₂Br (about 0.1-0.2%), HCF₂CH₂OH (0.2-0.8%), sulfolane (about 0.3-0.5%) and water (600-800 ppm). Further purification of the crude product was carried out using spinning band distillation at atmospheric pressure. The fraction having a boiling point between 106.5-106.7°C was collected and the impurity

profile was monitored using GC/MS (capillary column HP5MS, phenyl-methyl siloxane, Agilent19091S-433, 30.m, 250 μ m, 0.25 μ m; carrier gas - He, flow rate 1 mL/min; temperature program : 40°C, 4 min, temp. ramp 30°C/min, 5 230 °C, 20 min). Typically, the distillation of 240 g of crude product gave about 120 g of HCF₂CH₂OC(O)CH₃ of 99.89% purity, (250-300 ppm H₂O) and 80 g of material of 99.91% purity (containing about 280 ppm of water). Water was removed from the distilled product by treatment with 3A 10 molecular sieves, until water was not detectable by Karl Fischer titration (i.e., <1 ppm).

Preparation of 2,2-Difluoroethyl Propionate.

15 Potassium propionate (Aldrich, 99%) was dried at 100°C under a vacuum of 0.5-1 mm of Hg (66.7-133 Pa) for 4 to 5 h. The dried material had a water content of less than 5 ppm, as determined by Karl Fischer titration. In a dry box, 75 g (0.67 mol, 10 mol% excess) of the dried 20 potassium propionate was placed into a 500 mL, 3 neck round bottom flask containing a heavy magnetic stir bar. The flask was removed from the dry box, transferred into a fume hood, and equipped with a thermocouple well, a dry-ice condenser, and an additional funnel. Sulfolane (300 25 mL, Aldrich 99%, 600 ppm of water as determined by Karl Fischer titration) was melted and added to the 3 neck round bottom flask as a liquid under a flow of nitrogen. Agitation was started and the temperature of the reaction mixture was brought to about 100°C. HCF₂CH₂Br (87 g, 0.6 30 mol, E.I. du Pont de Nemours and Company, 99%) was placed

in the addition funnel and was slowly added to the reaction mixture. The addition was mildly exothermic and the temperature rose to 120-130°C in 15-20 min after the start of the addition. The addition of $\text{HCF}_2\text{CH}_2\text{Br}$ was kept
5 at a rate which maintained the internal temperature at 125-135°C. The addition took about 2-3 h. The reaction mixture was agitated at 120-130°C for an additional 6 h (typically the conversion of bromide at this point was about 90-95%). Then, the reaction mixture was cooled
10 down to room temperature and was agitated overnight. Next morning, heating was resumed for another 8 h.

At this point, the starting bromide and 1,1-difluoroethanol were not detectable in the crude reaction
15 mixture by NMR. The dry-ice condenser on the reaction flask was replaced by a hose adapter with a Teflon® valve and the flask was connected to a mechanical vacuum pump through a cold trap (-78°C, dry-ice/acetone). The reaction product was transferred into the cold trap at 40-
20 50°C under a vacuum of 1-2 mm Hg (133 to 266 Pa). The transfer took about 3 h and resulted in 48 g of crude $\text{HCF}_2\text{CH}_2\text{OC}(\text{O})\text{C}_2\text{H}_5$ of about 98% purity. Further purification of the crude product was carried out using spinning band distillation at atmospheric pressure. The fraction
25 having a boiling point between 120.3-120.6°C was collected and the impurity profile was monitored using GC/MS (capillary column HP5MS, phenyl-methyl siloxane, Agilent 19091S-433, 30 m, 250 µm, 0.25 µm; carrier gas - He, flow rate 1 mL/min; temperature program: 40°C, 4 min, temp.
30 ramp 30°C/min, 230°C, 20 min). The crude product (43 g)

had a purity of 99.91% and contained about 300 ppm of water. Water was removed from the product by treatment with 3A molecular sieves, until water was not detectable by Karl Fischer titration (i.e., <1 ppm).

5

HCF₂CH₂OC(O)C₂H₅: ¹H NMR (CDCl₃): 1.10 (3H, t), 2.35 (2H, q), 4.21 (2H, td), 5.87 (1H, tt) ppm; ¹⁹F NMR (CDCl₃): -125.68 (dt, 56.6, 13.7 Hz) ppm, GS/MS (m/z): 138 (M⁺, C₅H₈F₂O₂⁺).

10

Preparation of LiMn_{1.5}Ni_{0.42}Fe_{0.08}O₄ Cathode Active Material

For LiMn_{1.5}Ni_{0.42}Fe_{0.08}O₄, 401 g manganese (II) acetate tetrahydrate (Aldrich 63537), 115 g nickel (II) acetate tetrahydrate (Aldrich 72225) and 15.2 g iron (II) acetate anhydrous (Alfa Aesar 31140) were weighed into bottles on a balance then dissolved in 5 L of deionized water. KOH pellets were dissolved in 10 L of deionized water to produce a 3.0 M solution inside a 30 L reactor. The acetate solution was transferred to an addition funnel and dripped into the rapidly stirred reactor to precipitate the mixed hydroxide material. Once all 5 L of the acetate solution was added to the reactor stirring was continued for 1 h. Then stirring was stopped and the precipitate was allowed to settle overnight. After settling the liquid was removed from the reactor and 15 L of fresh deionized water was added. The contents of the reactor were stirred, allowed to settle again, and liquid removed. This rinse process was repeated. Then the precipitate was transferred to two (split evenly) coarse glass frit filtration funnels covered with Dacron[®] paper.

The solids were rinsed with deionized water until the filtrate pH reached 6 (pH of deionized rinse water), and a further 20 L of deionized water was added to each filter cake. Finally the cakes were dried in a vacuum oven at
5 120 °C overnight. The yield at this point was typically 80-90%.

The hydroxide precipitate was next ground and mixed with lithium carbonate. This step was done in 60 g
10 batches using a Fritsche Pulverisette automated mortar and pestle. For each batch the hydroxide mixture was weighed, then ground alone for 5 minutes in the Pulverisette. Then a stoichiometric amount with small excess of lithium carbonate was added to the system. For 53 g of hydroxide
15 11.2 g of lithium carbonate was added. Grinding was continued for a total of 60 minutes with stops every 10-15 minutes to scrape the material off of the surfaces of the mortar and pestle with a sharp metal spatula. If humidity caused the material to form clumps, it was sieved through
20 a 40 mesh screen once during grinding, then again following grinding.

The ground material was fired in air in a box furnace inside shallow rectangular alumina trays. The trays were
25 158 mm by 69 mm in size, and each held about 60 g of material. The firing procedure consisted of ramping from room temperature to 900 °C in 15 hours, holding at 900 °C for 12 hours, then cooling to room temperature in 15
hours.

30

Preparation of Nonaqueous Electrolyte Composition
Comprising 2,2-Difluoroethyl Acetate (DFEA) and Ethylene
Carbonate (EC)

5 2,2-Difluoroethyl acetate, prepared as described
above, was purified by spinning band distillation twice to
99.992% purity, as determined by gas chromatography using
a mass spectrometric detector. The purified 2,2-
difluoroethyl acetate and ethylene carbonate (anhydrous,
10 Novolyte, Independence, OH) were mixed together to make 15
mL of total solution in a 70:30 w/w ratio, and the
resulting mixture was dried over 3A molecular sieves
(Sigma-Aldrich, Milwaukee, WI). After drying, the water
content was determined to be 0.5 ppm using Karl Fischer
15 titration. The solution was syringe filtered through a
0.2 µm PTFE syringe filter. To 15.0 mL of the resulting
solution was added 2.28 g of lithium hexafluorophosphate
(battery grade, Novolyte) and the mixture was shaken for a
few minutes until all the solid was dissolved.

20

Preparation of Nonaqueous Electrolyte Composition
Comprising 2,2-Difluoroethyl Propionate (DFEP)

25 2,2-Difluoroethyl propionate, prepared as described
above, was purified by spinning band distillation twice to
99.990% purity, as determined by gas chromatography using
a mass spectrometric detector. The purified 2,2-
difluoroethyl propionate was dried over 3A molecular
sieves (Sigma-Aldrich, Milwaukee, WI). After drying, the
30 water content was determined to be <0.5 ppm using Karl

Fischer titration. The solution was syringe filtered through a 0.2 μm PTFE syringe filter. To the resulting DFEP (7.0 mL) was added a sufficient amount of lithium hexafluorophosphate (battery grade, Novolyte) to give a concentration of 1.0 M. The mixture was shaken for a few minutes until all the solid was dissolved.

Preparation of Nonaqueous Electrolyte Composition

10 Comprising 2,2-Difluoroethyl Propionate (DFEP) and Ethylene Carbonate (EC)

2,2-Difluoroethyl propionate, prepared as described above, was purified by spinning band distillation twice to 99.990% purity, as determined by gas chromatography using a mass spectrometric detector. The purified 2,2-difluoroethyl acetate and ethylene carbonate (anhydrous, Novolyte, Independence, OH) were mixed together to make 9.0 mL of total solution in a 70:30 w/w ratio, and the resulting mixture was dried over 3A molecular sieves (Sigma-Aldrich, Milwaukee, WI). After drying, the water content was determined to be <0.5 ppm using Karl Fischer titration. The solution was syringe filtered through a 0.2 μm PTFE syringe filter. To 9.0 mL of the resulting solution was added lithium hexafluorophosphate (battery grade, Novolyte) to give a concentration of 1.0 M. The mixture was shaken for a few minutes until all the solid was dissolved.

Preparation of an Iron-Doped, Lithium, Nickel, Manganese
Oxide (Fe-LNMO) Cathode

The following is a description of a representative preparation of an Fe-LNMO cathode. The cathode active material $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$, prepared as describe above, was ground for ten minutes using an agate mortar and pestle and then passed through a 75 μm sieve. Particle size was measured to be 18 μm (d90). The sized cathode active material (1.240 g), 0.155 g of Denka black (acetylene black, DENKA Corp., Japan), 1.292 g of polyvinylidene difluoride (PVDF) solution (12 wt% in *N*-methylpyrrolidone (NMP), Kureha America Inc., New York, NY, KFL#1120), and an additional 2.313 g of anhydrous NMP (Sigma -Aldrich, Milwaukee, WI) were mixed first using a planetary centrifugal mixer (THINKY ARE-310, THINKY Corp., Japan) at 2,000 rpm, a shear mixer (VWR, Wilmington, NC), and then a planetary centrifugal mixer at 2,000 rpm to form a uniform slurry. The slurry was coated on 25 μm thick aluminum foil using a doctor blade, dried on a hot plate at 100°C for five to seven minutes, then in a vacuum oven at 100°C for five to seven minutes. The resulting 25-mm wide cathode was placed on a 125 μm thick brass sheet and two 38 mm wide brass shim strips of 87 μm thickness were placed on either side of the cathode to control the gap thickness in the calender. The electrode and shims were covered with a second 125 μm thick brass sheet, and the assembly was passed through a calender three times using 100 mm diameter steel rolls heated to 125°C with a nip force of 154, 205, and 356 kg, respectively. The cathode was further dried in a vacuum

oven at 90°C at -25 inches of Hg (-85 kPa) for 15 h.

Preparation of a Lithium Titanate (LTO) Anode

5 The following is a description of a representative preparation of an LTO anode. The LTO anode active material, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (NEI Nanomyte™ BE-10, Somerset, NJ), was ground for ten minutes using an agate mortar and pestle. The ground anode active material (3.168 g), 0.396 g of Super P Li carbon (Timcal, Switzerland), 3.300 g of polyvinylidene difluoride (PVDF) solution (12 wt% in N-methylpyrrolidone (NMP), Kureha America Inc., New York, NY, KFL#1120), and an additional 4.136 g of NMP were mixed first using a planetary centrifugal mixer (THINKY ARE-310, 10 THINKY Corp., Japan) at 2,000 rpm, a shear mixer (VWR, 15 Wilmington, NC), and then a planetary centrifugal mixer at 2,000 rpm to form a uniform slurry. The slurry was coated on copper foil using a doctor blade, and dried first on a hot plate at 100°C for five to seven minutes, 20 then in a vacuum oven at 100°C for five to seven minutes. The resulting electrode was calendered at 125°C to constant thickness as previously described.

25 Fabrication of LTO|electrolyte|Fe-LNMO Full Cells

 The following is a description of a representative preparation of full cells containing an Fe-LNMO cathode, an LTO anode and an electrolyte composition. Circular anodes 15 mm in diameter and cathodes 14 mm in diameter 30 were punched out, placed in a heater in the antechamber of

a glove box, further dried under vacuum at 90°C for 15 h, and brought in to an argon glove box (Vacuum Atmospheres, Hawthorne, CA, Nexus purifier). Nonaqueous electrolyte lithium-ion CR2032 coin cells were prepared for
5 electrochemical evaluation. The coin cell parts (stainless steel case, two spacers, wave spring, lid, and polypropylene gasket) and coin cell crimper were obtained from Hohsen Corp (Osaka, Japan). An Fe-LNMO cathode, prepared as described above, a Celgard® separator 2325
10 (Celgard, LLC. Charlotte, NC), an LTO anode, prepared as described above, and a few drops of the nonaqueous electrolyte composition of interest, were assembled to form the LTO/Fe-LNMO full cells.

15

COMPARATIVE EXAMPLE 1 AND WORKING EXAMPLES 1-2

High Temperature Performance of Full Cells

Full cells, containing the anode, cathode, and nonaqueous electrolyte shown in Table 1, were cycled using
20 a commercial battery tester (Series 4000, Maccor, Tulsa, OK) in a temperature-controlled chamber at 55 °C using voltage limits of 1.9 to 3.4 V. The constant-current charge and discharge currents for the first two cycles were 12 mA/g of LNMO (about 0.1C rate), and subsequent
25 cycles were carried out at 120 mA/g of LNMO for 29 cycles (about 1C rate) then one cycle at 12 mA/g then repeated until T80 was reached. T80 is defined as the number of cycles before the cell's discharge capacity has been reduced to 80% of the initial discharge capacity of the
30 third charge-discharge cycle (first cycle at the 1C rate).

The cycle number at which T80 was reached is also shown in Table 1.

As can be seen from the data in Table 1, the cycle number obtained with the full cells containing 2,2-difluoroethyl propionate or 2,2-difluoroethyl propionate and ethylene carbonate (Examples 1 and 2) were higher than the cycle number obtained with the full cell containing 2,2-difluoroethyl acetate and ethylene carbonate (Comparative Example 1).

15

Table 1

High Temperature Performance of Full Cells

| | Anode / Cathode | Electrolyte | Cycle No. to T80 |
|--------------------------|--------------------|-------------|---------------------|
| Comparative Example 1 | LTO / Fe-LNMO | DFEA + EC | 51 |
| Example 1 | LTO / Fe-LNMO | DFEP | 75 |
| Example 2 | LTO / Fe-LNMO | DFEP + EC | 87 |

CLAIMS

What is claimed is:

5

1. An electrolyte composition comprising (a) at least one electrolyte salt, and (b) at least one fluorine-containing carboxylic acid ester represented by the formula $R^1-C(O)O-R^2$, wherein

- 10 R^1 is CH_3CH_2- and R^2 is $-CH_2CHF_2$,
 R^1 is CH_3- and R^2 is $-CH_2CH_2CHF_2$,
 R^1 is CH_3CH_2- and R^2 is $-CH_2CH_2CHF_2$,
 R^1 is $CHF_2CH_2CH_2-$ and R^2 is $-CH_2CH_3$, or
 R^1 is CHF_2CH_2- and R^2 is $-CH_2CH_3$.

15

2. The electrolyte composition of claim 1, wherein the fluorine-containing carboxylic acid ester is $CH_3CH_2-COO-CH_2CF_2H$.

20

3. The electrolyte composition of claim 1, wherein the fluorine-containing carboxylic acid ester is $CH_3-COO-CH_2CH_2CF_2H$

25

4. The electrolyte composition of claim 1 further comprising at least one carbonate co-solvent.

30

5. The electrolyte composition of claim 4 wherein the carbonate co-solvent is selected from the group consisting of ethyl methyl carbonate, dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene

carbonate, vinylethylene carbonate, fluoroethylene carbonate, 2,2,2-trifluoroethyl carbonate, and methyl 2,2,3,3-tetrafluoropropyl carbonate.

5 6. The electrolyte composition of claim 1 wherein the electrolyte salt is selected from one or more members of the group consisting of:

 lithium hexafluorophosphate,
 Li PF₃(CF₂CF₃)₃,
10 lithium bis(trifluoromethanesulfonyl)imide,
 lithium bis(perfluoroethanesulfonyl)imide,
 lithium (fluorosulfonyl)
 (nonafluorobutanesulfonyl)imide,
 lithium bis(fluorosulfonyl)imide,
15 lithium tetrafluoroborate,
 lithium perchlorate,
 lithium hexafluoroarsenate,
 lithium trifluoromethanesulfonate,
 lithium tris(trifluoromethanesulfonyl)methide,
20 lithium bis(oxalato)borate,
 lithium difluoro(oxalato)borate,
 Li₂B₁₂F_{12-x}H_x where x is equal to 0 to 8, and
 a mixture of lithium fluoride and an anion receptor.

25 7. The electrolyte composition of claim 6 wherein the electrolyte salt is lithium hexafluorophosphate.

 8. The electrolyte composition of claim 1 further comprising at least one film-forming additive.

30

9. The electrolyte composition of claim 8, wherein the film-forming additive comprises fluoroethylene carbonate.

- 5 10. An electrochemical cell comprising:
- (a) a housing;
 - (b) an anode and a cathode disposed in said housing and in ionically conductive contact with one another;
 - (c) an electrolyte composition disposed in said
- 10 housing and providing an ionically conductive pathway between said anode and said cathode, wherein the electrolyte composition comprises:
- (i) at least one electrolyte salt; and
 - (ii) at least one fluorine-containing carboxylic
- 15 acid ester represented by the formula $R^1-C(O)O-R^2$, wherein
- R^1 is CH_3CH_2- and R^2 is $-CH_2CHF_2$,
 - R^1 is CH_3- and R^2 is $-CH_2CH_2CHF_2$,
 - R^1 is CH_3CH_2- and R^2 is $-CH_2CH_2CHF_2$,
 - 20 R^1 is $CHF_2CH_2CH_2-$ and R^2 is $-CH_2CH_3$, or
 - R^1 is CHF_2CH_2- and R^2 is $-CH_2CH_3$; and
- (d) a porous separator between said anode and said cathode.

- 25 11. The electrochemical cell of claim 10, wherein the electrolyte composition further comprises at least one carbonate co-solvent.

- 30 12. The electrochemical cell of claim 11 wherein the carbonate co-solvent is selected from the group consisting

of ethyl methyl carbonate, dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene carbonate, vinylene carbonate, fluoroethylene carbonate, 2,2,2-trifluoroethyl carbonate, and methyl 2,2,3,3-tetrafluoropropyl carbonate.

13. The electrochemical cell of claim 10, wherein said electrochemical cell is a lithium ion battery.

14. The lithium ion battery of claim 13, wherein the anode is lithium titanate or graphite.

15. The lithium ion battery of claim 13, wherein the cathode comprises a cathode active material exhibiting greater than 30 mAh/g capacity in the potential range greater than 4.6 V versus lithium metal.

16. The lithium ion battery of claim 13, wherein the cathode comprises a lithium-containing manganese composite oxide having a spinel structure as active material, the lithium-containing manganese composite oxide being represented by the formula:



wherein x is 0.03 to 1.0; x changes in accordance with release and uptake of lithium ions and electrons during charge and discharge; y is 0.3 to 0.6; M comprises one or more of Cr, Fe, Co, Li, Al, Ga, Nb, Mo, Ti, Zr, Mg, Zn, V, and Cu; z is 0.01 to 0.18, and d is 0 to 0.3.

17. The lithium ion battery of claim 16, wherein y

is 0.38 to 0.48, z is 0.03 to 0.12, and d is 0 to 0.1.

18. The lithium ion battery of claim 16, wherein M is one or more of Li, Cr, Fe, Co, and Ga.

5

19. An electronic device comprising an electrochemical cell according to Claim 10.

INTERNATIONAL SEARCH REPORT

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|---|
| International application No PCT/US2013/029825 |
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A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M10/0569 H01M10/052 H01M6/16
 ADD. H01M10/0568 H01M10/0567 H01M10/0525 H01M4/485 H01M4/505
 H01M4/587

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, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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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

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"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)

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"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

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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

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Date of the actual completion of the international search

2 May 2013

Date of mailing of the international search report

14/05/2013

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INTERNATIONAL SEARCH REPORT

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