(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 June 2017 (29.06.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/112424 A1

(51) International Patent Classification:
H01M 4/485 (2010.01) ***H01M 10/0525*** (2010.01)
H01M 4/505 (2010.01) ***H01M 10/0567*** (2010.01)
H01M 4/525 (2010.01) ***H01M 10/0569*** (2010.01)
H01M 4/587 (2010.01)

(21) International Application Number:
PCT/US2016/065585

(22) International Filing Date:
8 December 2016 (08.12.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/270,676 22 December 2015 (22.12.2015) US

(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; Chestnut Run Plaza, 974 Centre Road, P. O. Box 2915, Wilmington, Delaware 19805 (US).

(72) Inventors: **KOURTAKIS, Kostantinos**; 804 Springlawn Drive, Media, Pennsylvania 19063 (US). **GRIER, Gerard Joseph**; 223 Steeplechase Circle, Wilmington, Delaware 19808 (US). **SUBRAMONEY, Shekhar**; 425 Stella Drive, Hockessin, Delaware 19707 (US). **ZHANG, Lei**; 411 Bartram Lane West, Hockessin, Delaware 19707 (US).

(74) Agent: **BREIKSS, Anne I.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, Chestnut Run Plaza 721/2340, 974 Centre Road, PO Box 2915, Wilmington, Delaware 19805 (US).

(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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, SA, 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, ST, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: ELECTROLYTE COMPOSITIONS COMPRISING METAL FLUORIDE PARTICLES

(57) Abstract: Disclosed herein are electrolyte compositions comprising a liquid medium comprising at least one non-aqueous solvent; inorganic particles comprising at least one Group 2 metal fluoride and having an average primary median particle diameter d?50#191 in the range of about 1 nm to about 700 nm as determined by dynamic light scattering; and at least one electrolyte salt. The inorganic particles and the liquid medium form a suspension. The electrolyte compositions are useful in electrochemical cells, such as lithium ion batteries.

WO 2017/112424 A1

TITLE

ELECTROLYTE COMPOSITIONS COMPRISING METAL FLUORIDE PARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority of United States Provisional Application No. 62/270,676 filed on December 22, 2015, the entire disclosure of which is hereby incorporated by reference.

FIELD OF DISCLOSURE

The disclosure herein relates to electrolyte compositions comprising a liquid medium comprising at least one non-aqueous solvent and inorganic particles comprising at least one Group 2 metal fluoride, wherein the inorganic particles and the liquid medium form a suspension. The electrolyte compositions are useful in electrochemical cells, such as lithium ion batteries.

BACKGROUND

With the advancement in portable electronic devices and intense interest in plug-in hybrid electric vehicles, there is great demand to increase the energy and power capabilities of lithium ion batteries. In this regard, increasing the operational voltage is a viable strategy. Current lithium ion battery electrolyte solvents typically contain one or more linear carbonates, such as ethyl methyl carbonate, dimethyl carbonate, or diethyl carbonate; and a carbonate, such as ethylene carbonate. However, at cathode potentials above 4.2 V these electrolytes can decompose, which can result in a loss of battery performance. What is needed are electrolyte solvents, and compositions thereof, that will have improved cycling performance at high temperature when used in a lithium ion battery, particularly such a battery that operates at high voltage (*i.e.* up to about 5 V), or that incorporates a high voltage cathode.

SUMMARY

In one embodiment, there is provided herein an electrolyte composition comprising:

a) a liquid medium comprising at least one non-aqueous solvent;

b) inorganic particles comprising at least one Group 2 metal fluoride and having an average primary median particle diameter d_{50} in the range of about 1 nm to about 700 nm as determined by dynamic light scattering; and

c) at least one electrolyte salt;

wherein the inorganic particles and the liquid medium form a suspension.

In one embodiment, the non-aqueous solvent comprises at least one carbonate. In one embodiment, the non-aqueous solvent comprises at least one fluorinated solvent. In some embodiments, the suspension is a colloidal suspension. In some embodiments, the Group 2 metal fluoride is selected from the group consisting of MgF_2, CaF_2, SrF_2, BaF_2, and mixtures thereof. In one embodiment, the Group 2 metal fluoride comprises MgF_2.

In another embodiment there is provided herein an electrochemical cell comprising an electrolyte composition as disclosed herein. In a further embodiment, the electrochemical cell is a lithium ion battery.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the X-ray photoelectron spectroscopy depth profile of in-depth composition (atom%) from the anode of Example 3 after cycling.

Figure 2 shows the X-ray photoelectron spectroscopy depth profile of in-depth composition (atom%) from the cathode of Example 3 after cycling.

Figure 3 shows the X-ray photoelectron spectroscopy depth profile of in-depth composition (atom%) from the anode of Example 5 after cycling.

Figure 4 shows the X-ray photoelectron spectroscopy depth profile of in-depth composition (atom%) from the cathode of Example 5 after cycling.

Figure 5 represents a high-resolution transmission electron microscopy image of the anode interface of the solid electrolyte interphase (SEI) of Example 3.

Figure 6 shows the selected area electron diffraction pattern of the anode interface or the SEI of Example 3.

Figure 7 represents a high angle annular dark field image of the anode interface of the SEI from Example 3, and a region (the area designated by the square) which was analyzed by energy dispersive spectroscopy (left, same section as shown in Figure 6).

Figure 8 shows a graphical representation of the results from energy dispersive spectroscopy of the anode interface of Example 3 within the area of the square shown in Figure 7.

Figure 9 shows a high angle annular dark field image of the cathode interface from Example 3. The image shows two regions which were analyzed by electron dispersive spectroscopy, shown in the areas of the squares labeled 1 and 2.

Figure 10 shows a graphical representation of the results from energy dispersive spectroscopy of the cathode interface of Example 3 within the area of square 1 shown in Figure 9.

Figure 11 shows a graphical representation of the results from energy dispersive spectroscopy of the cathode interface of Example 3 within the area of square 2 shown in Figure 9.

DETAILED DESCRIPTION

The features and advantages of the present disclosure will be more readily understood by those of ordinary skill in the art from reading the following detailed description. It is to be appreciated that certain features of the disclosure, which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single element. Conversely, various features of the disclosure that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. In addition, references to the singular may also include the plural (for example, “a” and “an” may refer to one or more) unless the context specifically states otherwise.

The use of numerical values in the various ranges specified in this application, unless expressly indicated otherwise, are stated as approximations as though the minimum and maximum values within the stated ranges were both proceeded by the word “about”. In this manner, slight variations above and below the stated ranges can be used to achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including each and every value between the minimum and maximum values.

As used above and throughout the disclosure, 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.

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.

The term “anode”, as used herein, 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.

The term “lithium ion battery”, as used herein, 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.

Equilibrium potential between lithium and lithium ion is the potential of a reference electrode using lithium metal in contact with the non-aqueous electrolyte containing lithium salt at a concentration sufficient to give about 1 mole/liter of lithium ion concentration, and subjected to sufficiently small currents so that the potential of the reference electrode is not significantly altered from its equilibrium value (Li/Li^+). The potential of such a Li/Li^+ reference electrode is assigned here the value of 0.0V. Potential of an anode or cathode means the potential difference between the anode or cathode and that of a Li/Li^+ reference electrode. Herein voltage means the voltage difference between the cathode and the anode of a cell, neither electrode of which may be operating at a potential of 0.0V.

The term “SEI”, as used herein, refers to a solid electrolyte interphase layer formed on the active material of an electrode. A lithium-ion secondary electrochemical cell is assembled in an uncharged state and must be charged (a process called formation) for use. During the first few charging events (battery formation) of a lithium-ion secondary electrochemical cell, components of the electrolyte are reduced or otherwise decomposed or incorporated onto the surface of the negative active material and oxidized or otherwise decomposed or incorporated onto the surface of the positive active material, electrochemically forming a solid-electrolyte interphase on the active materials. These layers, which are electrically insulating but ionically conducting, help prevent decomposition of the electrolyte and can extend the cycle life and improve the performance of the battery. On the anode, the SEI can suppress the reductive decomposition of the electrolyte; on the cathode, the SEI can suppress the oxidation of the electrolyte components.

The term “alkyl group”, as used herein, refers to a saturated linear or branched chain hydrocarbon radical containing from 1 to 10 carbon atoms. Examples of alkyl groups include methyl, ethyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isoamyl, hexyl, heptyl, and octyl.

The term “fluoroalkyl group”, as used herein, refers to an alkyl group wherein at least one hydrogen is replaced by fluorine.

The term “carbonate” as used herein refers specifically to an organic carbonate, wherein the organic carbonate is a dialkyl diester derivative of carbonic acid, the organic carbonate having a general formula $R'OCOOR''$, wherein R' and R'' are each independently selected from alkyl groups having at least 1 carbon atom, wherein the alkyl substituents can be the same or different, can be saturated or unsaturated, substituted or unsubstituted, can form a cyclic structure via interconnected atoms, or include a cyclic structure as a substituent of either or both of the alkyl groups.

Disclosed herein are electrolyte compositions comprising:

a) a liquid medium comprising at least one non-aqueous solvent;

b) inorganic particles comprising at least one Group 2 metal fluoride and having an average primary median particle diameter d_{50} in the range of about 1 nm to about 700 nm as determined by dynamic light scattering; and

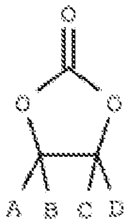
c) at least one electrolyte salt;

wherein the inorganic particles and the liquid medium form a suspension. The electrolyte compositions are useful in electrochemical cells, particularly lithium ion batteries. It has been found that such electrolyte compositions can provide a secondary battery having a high energy density with improved cycling performance at high temperature. During battery formation, at least a portion of the inorganic particles react or are incorporated into the SEI layer of one or both electrodes.

In one embodiment, the non-aqueous solvent comprises at least one carbonate. In another embodiment, the non-aqueous solvent comprises at least one non-fluorinated carbonate. Suitable non-fluorinated carbonates include ethylene carbonate, ethyl methyl carbonate, dimethyl carbonate, diethyl carbonate, vinylene carbonate, di-tert-butyl carbonate, vinylethylene carbonate, dimethylvinylene carbonate, propylene carbonate, ethyl propyl vinylene carbonate, dimethylvinylene carbonate, or mixtures thereof. In one embodiment the non-fluorinated carbonate comprises ethylene carbonate, propylene carbonate, or mixtures thereof. In one embodiment, the non-fluorinated carbonate comprises ethylene carbonate. In one embodiment, the non-fluorinated carbonate comprises propylene carbonate. In one embodiment, the non-fluorinated carbonate comprises ethyl methyl carbonate. In one embodiment, the non-fluorinated carbonate comprises dimethyl carbonate.

In the electrolyte compositions disclosed herein, the non-fluorinated carbonate or mixtures thereof can be used in various amounts depending on the desired properties of the electrolyte composition. In one embodiment, the non-fluorinated carbonate(s) in combination is present in the electrolyte composition in the range of about 0.5 percent to about 95 percent by weight of the electrolyte composition, or about 5 percent to about 95 percent, or about 10 percent to about 80 percent, about 20 percent to about 40 percent, or about 25 percent to about 35 percent by weight of the electrolyte composition. In another embodiment, the non-fluorinated carbonate is present in the range of about 0.5 percent to about 10 percent by weight, or about 1 percent to about 10 percent, or about 5 percent to about 10 percent by weight of the electrolyte composition.

In one embodiment, the non-aqueous solvent comprises a cyclic fluorinated carbonate. Suitable cyclic fluorinated carbonates can be represented by the following structure



wherein

i) each of A, B, C, and D is H, F, a saturated or unsaturated C_1 to C_4 alkyl group, or a saturated or unsaturated C_1 to C_4 fluoroalkyl group, and can be the same as or different from each other; and

ii) at least one of A, B, C, and D comprises fluorine.

The term “unsaturated”, as used herein, refers to an olefinically unsaturated group containing at least one carbon-carbon double bond.

Suitable cyclic fluorinated carbonates include 4-fluoroethylene carbonate (abbreviated as FEC, also known as 4-fluoro-1,3-dioxolan-2-one), difluoroethylene carbonate isomers, trifluoroethylene carbonate isomers, tetrafluoroethylene carbonate, 2,2,3,3-tetrafluoropropyl methyl carbonate, bis(2,2,3,3-tetrafluoropropyl) carbonate, bis(2,2,2-trifluoroethyl) carbonate, 2,2,2-trifluoroethyl methyl carbonate, bis(2,2-difluoroethyl) carbonate, 2,2-difluoroethyl methyl carbonate, methyl 2,3,3-trifluoroallyl carbonate, or mixtures thereof. In one embodiment the fluorinated carbonate comprises fluoroethylene carbonate. In one embodiment, the fluorinated carbonate comprises 4-fluoro-1,3-dioxolan-2-one; 4,5-difluoro -1,3-dioxolan-2-one; 4,5-difluoro-4-methyl-1,3-dioxolan-2-one; 4,5-difluoro-4,5-dimethyl-1,3-dioxolan-2-one; 4,4-difluoro-1,3-dioxolan-2-one; 4,4,5-trifluoro-1,3-dioxolan-2-one; or mixtures thereof.

In the electrolyte compositions disclosed herein, the cyclic fluorinated carbonate can be used in various amounts depending on the desired properties of the electrolyte composition. In one embodiment, the cyclic fluorinated carbonate is present in the electrolyte composition in the range of about 0.5 percent by weight to about 40 percent by weight of the electrolyte composition, or about 1 to about 30, or about 1 to about 25, based on the total weight of the electrolyte composition. In some embodiments, the cyclic fluorinated carbonate is present in the electrolyte composition in a percentage by weight that is defined by a lower limit and an upper limit. The lower limit of the range is 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6, 7, 8, 9, 10, 11, 12, 13, or 14 and the upper limit of the range is 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, or 40. All percentages by weight are based on the total weight of the electrolyte composition.

In one embodiment, the non-aqueous solvent comprises at least one carbonate, and the carbonate comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, vinylene carbonate, 4-fluoroethylene carbonate, or a mixture thereof.

In another embodiment, the non-aqueous solvent comprises at least one fluorinated solvent. In one embodiment, the fluorinated solvent is a fluorinated acyclic carboxylic acid ester. In one embodiment, the fluorinated solvent is a fluorinated acyclic carbonate. In one embodiment, the fluorinated solvent is a fluorinated acyclic ether. In another embodiment, the fluorinated solvent comprises 2,2-difluoroethyl acetate or 2,2-difluoroethyl methyl carbonate.

Suitable fluorinated acyclic carboxylic acid esters are represented by the formula

$$R^1\text{-COO-}R^2$$

wherein

i) R^1 is H, an alkyl group, or a fluoroalkyl group;

ii) R^2 is an alkyl group or a fluoroalkyl group;

iii) either or both of R^1 and R^2 comprises fluorine; and

iv) R^1 and R^2, taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms.

In one embodiment, R^1 is H and R^2 is a fluoroalkyl group. In one embodiment, R^1 is an alkyl group and R^2 is a fluoroalkyl group. In one embodiment, R^1 is a fluoroalkyl group and R^2 is an alkyl group. In one embodiment, R^1 is a fluoroalkyl group and R^2 is a fluoroalkyl group, and R^1 and R^2 can be either the same as or different from each other. In one embodiment, R^1 comprises one carbon atom. In one embodiment, R^1 comprises two carbon atoms.

In another embodiment, R^1 and R^2 are as defined herein above, and R^1 and R^2, taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms and further comprise at least two fluorine atoms, with the proviso that neither R^1 nor R^2 contains a FCH_2- group or a –FCH- group.

Examples of suitable fluorinated acyclic carboxylic acid esters include without limitation CH_3-COO-CH_2CF_2H (2,2-difluoroethyl acetate, CAS No. 1550-44-3), CH_3-COO-CH_2CF_3 (2,2,2-trifluoroethyl acetate, CAS No. 406-95-1), CH_3CH_2-COO-CH_2CF_2H (2,2-difluoroethyl propionate, CAS No. 1133129-90-4), CH_3-COO-$CH_2CH_2CF_2H$ (3,3-difluoropropyl acetate), CH_3CH_2-COO-$CH_2CH_2CF_2H$ (3,3-difluoropropyl propionate), HCF_2-CH_2-CH_2-COO-CH_2CH_3 (ethyl 4,4-difluorobutanoate, CAS No. 1240725-43-2), H-COO-CH_2CF_2H (difluoroethyl formate, CAS No. 1137875-58-1), H-COO-CH_2CF_3 (trifluoroethyl formate, CAS No. 32042-38-9), F_2CHCH_2-COO-CH_3 (methyl 3,3-difluoropropionate), F_2CHCH_2-COO-CH_2CH_3 (ethyl

3,3-difluoropropionate), and mixtures thereof. In one embodiment, the fluorinated acyclic carboxylic acid ester comprises 2,2-difluoroethyl acetate (CH_3-COO-CH_2CF_2H). In one embodiment, the fluorinated acyclic carboxylic acid ester comprises 2,2-difluoroethyl propionate (CH_3CH_2-COO-CH_2CF_2H). In one embodiment, the fluorinated acyclic carboxylic acid ester comprises 2,2,2-trifluoroethyl acetate (CH_3-COO-CH_2CF_3). In one embodiment, the fluorinated acyclic carboxylic acid ester comprises 2,2-difluoroethyl formate (H-COO-CH_2CF_2H).

Suitable fluorinated acyclic carbonates are represented by the formula

$$R^3\text{-OCOO-}R^4$$

wherein

i) R^3 is a fluoroalkyl group;

ii) R^4 is an alkyl group or a fluoroalkyl group; and

iii) R^3 and R^4 taken as a pair comprise at least two carbon atoms but not more than seven carbon atoms.

In one embodiment, R^3 is a fluoroalkyl group and R^4 is an alkyl group. In one embodiment, R^3 is a fluoroalkyl group and R^4 is a fluoroalkyl group, and R^3 and R^4 can be either the same as or different from each other. In one embodiment, R^3 comprises one carbon atom. In one embodiment, R^3 comprises two carbon atoms.

In another embodiment, R^3 and R^4 are as defined herein above, and R^3 and R^4, taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms and further comprise at least two fluorine atoms, with the proviso that neither R^3 nor R^4 contains a FCH_2- group or a –FCH- group.

Examples of suitable fluorinated acyclic carbonates include without limitation CH_3-OC(O)O-CH_2CF_2H (methyl 2,2-difluoroethyl carbonate, CAS No. 916678-13-2), CH_3-OC(O)O-CH_2CF_3 (methyl 2,2,2-trifluoroethyl carbonate, CAS No. 156783-95-8), CH_3-OC(O)O-$CH_2CF_2CF_2H$ (methyl 2,2,3,3-tetrafluoropropyl carbonate, CAS No.156783-98-1), HCF_2CH_2-OCOO-CH_2CH_3 (2,2-difluoroethyl ethyl carbonate, CAS No. 916678-14-3), and CF_3CH_2-OCOO-CH_2CH_3 (2,2,2-trifluoroethyl ethyl carbonate, CAS No. 156783-96-9).

Suitable fluorinated acyclic ethers are represented by the formula

$$R^5\text{-O-}R^6$$

wherein

i) R^5 is a fluoroalkyl group;

ii) R^6 is an alkyl group or a fluoroalkyl group; and

iii) R^5 and R^6 taken as a pair comprise at least two carbon atoms but not more than seven carbon atoms.

In one embodiment, R^5 is a fluoroalkyl group and R^6 is an alkyl group. In one embodiment, R^5 is a fluoroalkyl group and R^6 is a fluoroalkyl group, and R^5 and R^6 can be either the same as or different from each other. In one embodiment, R^5 comprises one carbon atom. In one embodiment, R^5 comprises two carbon atoms.

In another embodiment, R^5 and R^6 are as defined herein above, and R^5 and R^6, taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms and further comprise at least two fluorine atoms, with the proviso that neither R^5 nor R^6 contains a FCH_2- group or a –FCH- group.

Examples of suitable fluorinated acyclic ethers include without limitation $HCF_2CF_2CH_2$-O-CF_2CF_2H (CAS No. 16627-68-2) and HCF_2CH_2-O-CF_2CF_2H (CAS No. 50807-77-7).

The fluorinated solvent may comprise a fluorinated acyclic carboxylic acid ester, a fluorinated acyclic carbonate, a fluorinated acyclic ether, or mixtures thereof. As used herein, the term “mixtures thereof” encompasses both mixtures within and mixtures between solvent classes, for example mixtures of two or more fluorinated acyclic carboxylic acid esters, and also mixtures of fluorinated acyclic carboxylic acid esters and fluorinated acyclic carbonates, for example. Non-limiting examples include a mixture of 2,2-difluoroethyl acetate and 2,2-difluoroethyl propionate; and a mixture of 2,2-difluoroethyl acetate and 2,2-difluoroethyl methyl carbonate.

In one embodiment, the fluorinated solvent is:

a) a fluorinated acyclic carboxylic acid ester represented by the formula:

$$R^1\text{-COO-}R^2,$$

b) a fluorinated acyclic carbonate represented by the formula:

$$R^3\text{-OCOO-}R^4,$$

c) a fluorinated acyclic ether represented by the formula:

$$R^5\text{-O-}R^6,$$

or mixtures thereof;

wherein

i) R^1 is H, an alkyl group, or a fluoroalkyl group;

ii) R^3 and R^5 is each independently a fluoroalkyl group and can be either the same as or different from each other;

iii) R^2, R^4, and R^6 is each independently an alkyl group or a fluoroalkyl group and can be either the same as or different from each other;

iv) either or both of R^1 and R^2 comprises fluorine; and

v) R^1 and R^2, R^3 and R^4, and R^5 and R^6, each taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms.

In another embodiment, the fluorinated solvent is

a) a fluorinated acyclic carboxylic acid ester represented by the formula:

$$R^1\text{-COO-}R^2,$$

b) a fluorinated acyclic carbonate represented by the formula:

$$R^3\text{-OCOO-}R^4,$$

c) a fluorinated acyclic ether represented by the formula:

$$R^5\text{-O-}R^6,$$

or mixtures thereof;

wherein

i) R^1 is H, an alkyl group, or a fluoroalkyl group;

ii) R^3 and R^5 is each independently a fluoroalkyl group and can be either the same as or different from each other;

iii) R^2, R^4, and R^6 is each independently an alkyl group or a fluoroalkyl group and can be either the same as or different from each other;

iv) either or both of R^1 and R^2 comprises fluorine; and

v) R^1 and R^2, R^3 and R^4, and R^5 and R^6, each taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms and further comprise at least two fluorine atoms, with the proviso that none of R^1, R^2, R^3, R^4, R^5, nor R^6 contains a FCH_2- group or a –FCH- group.

In the electrolyte compositions disclosed herein, the fluorinated solvent or mixtures thereof can be used in various amounts depending on the desired properties of the electrolyte composition. In some embodiments, the electrolyte composition comprises from about 5 weight percent to about 95 weight percent of the fluorinated solvent. In some embodiments, the electrolyte composition comprises from about 10 weight percent to about 90 weight percent, or from about 10 weight percent to about 80 weight percent, or from about 20 weight percent to about 80 weight percent, or from about 30 weight percent to about 80 weight percent, or from about 40 weight percent to about 80 weight percent, or from about 50 weight percent to about 80 weight percent, or from about 60 weight percent to about 80 weight percent fluorinated solvent. In some embodiments, the fluorinated solvent is present in the electrolyte composition in a percentage by weight that is defined by a lower limit and an upper limit. The lower limit of the range is 5, 10, 20, 25, 30, 35, 40, 45, 50, 55, 60, or 65 and the upper limit of the range is 70, 75, 80, 85, 90, 95, 96, 97, 98, or 99. All percentages by weight are based on the total weight of the electrolyte composition.

Fluorinated acyclic carboxylic acid esters, fluorinated acyclic carbonates, and fluorinated acyclic ethers suitable for use herein may be prepared using known methods. 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 can be prepared using the method described in the Examples herein below. Other fluorinated acyclic carboxylic acid esters may be prepared using the same method using different starting carboxylate salts. Similarly, methyl chloroformate may be reacted with 2,2-difluoroethanol to form methyl 2,2-difluoroethyl carbonate. Synthesis of $HCF_2CF_2CH_2$-O-CF_2CF_2H can be done by reacting 2,2,3,3-tetrafluoropropanol with tetrafluoroethylene in the presence of base (e.g., NaH, etc.). Similarly, reaction of 2,2-difluoroethanol with tetrafluoroethylene yields HCF_2CH_2-O-CF_2CF_2H. Alternatively, some of the fluorinated solvents disclosed herein may be obtained commercially. For best results, it is desirable to purify the fluorinated acyclic carboxylic esters and fluorinated acyclic carbonates to a purity level of at least about 99.9%, for example at least about 99.99%. The fluorinated solvents disclosed herein may be purified using distillation methods such as vacuum distillation or spinning band distillation.

The electrolyte compositions comprise inorganic particles comprising at least one Group 2 metal fluoride. Suitable Group 2 metal fluorides include magnesium fluoride (MgF_2), calcium fluoride (CaF_2), strontium fluoride (SrF_2), barium fluoride (BaF_2), and mixtures thereof. The particles may contain one or more distinct phases of Mg, Ca, Sr, Ba, and F. The particles can contain these phases as core shell phases, graded compositions, or other structures within the particles. The particles typically have an average primary median particle diameter d_{50} of about 1 nm to about 700 nm, or about 1 nm to about 600 nm, or about 1 nm to 500 nm or about 1 nm to about 400 nm, or about 1 nm to about 300 nm, or about 1 nm to about 200 nm, or about 1 nm to about 100 nm, or less than about 700 nm, or less than about 600 nm, or less than about 500 nm, or less than about 450 nm, or less than about 350 nm, or less than about 250 nm, or less than about 150 nm, or less than about 100 nm, as determined by dynamic light scattering. In one embodiment, the particles can be aggregated in the final electrolyte formulation, with the median size of the aggregate having the diameters listed above. The inorganic particles may be obtained commercially or prepared using methods known in the art.

The electrolyte composition can comprise an amount of the inorganic particles in the range of about 0.01 weight percent to about 10 weight percent, based on the total weight of the electrolyte composition. In another embodiment, the electrolyte composition can comprise an amount of the inorganic particles in the range of about 0.05 to about 5 weight percent, based on the total weight of the electrolyte composition. In other embodiments, the electrolyte composition comprises an amount of the inorganic particles in a percentage by weight range that is defined by a lower limit and an upper limit. The lower limit of the range is 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 3.5, 4.0, or 4.5, and the upper limit of the range is 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, or 10. All percentages by weight are based on the total weight of the electrolyte composition.

The inorganic particles can be any shape, for example spherical, oblong, needle-like, platelet, or pyramidal, and can be mixtures of different shapes. The particles can be solid or hollow, and can also comprise mixtures of Group 2 metal fluorides within a particle or solid solutions of fluoride phases within a particle. Mixtures of inorganic particles of different Group 2 metal fluorides can also be used, for example mixtures of two or more of MgF_2, CaF_2, SrF_2, and BaF_2. In one embodiment, the electrolyte composition comprises MgF_2 particles. In one embodiment, the electrolyte composition comprises CaF_2 particles. In one embodiment, the electrolyte composition comprises SrF_2 particles. In one embodiment, the electrolyte composition comprises BaF_2 particles. In another embodiment, the electrolyte composition comprises inorganic particles comprising at least one Group 2 metal fluoride, wherein the Group 2 metal fluoride is selected from the group consisting of MgF_2, CaF_2, SrF_2, BaF_2, and mixtures thereof.

Optionally, the inorganic particles can be treated with chemical reagents to obtain treated inorganic particles having at least a portion of their surface functionalized with an electrochemically unstable functional group. By “electrochemically unstable functional group” it is meant a functional group that may decompose or react during use in an electrochemical battery or cell, but which also can help in stabilizing the inorganic particles in the electrolyte before use in the electrochemical cell.

Suitable electrochemically unstable functional groups include functional groups derived from one or more of acrylate, methacrylate, or olefin. In one embodiment, the inorganic particles are surface functionalized with one or more silanes, wherein silanes have at least one acryloyloxy, methacryloyloxy, or vinyl functional group.

The acryloyloxy and methacryloyloxy groups contain the functional group CH_2=CH_2-C(O)O- with optional alkyl substitutions, such as methacrylic functionalities. Specifically, the functional group can be represented by the formula X-Y-Si-. While not being bound by theory, the fragment may be covalently grafted to the surface of the nanoparticles using the reaction of surface hydroxyls with silanes of the type X–Y–$SiR^7R^8R^9$. X represents an acryloyloxy (CH_2=CHC(=O)O-) or methacryloyloxy (CH_2=C(CH_3)C(=O)O-) functional group. Y represents a divalent organic radical covalently bonded to the acryloyloxy or methacryloyloxy functional group and the silane functional group. Examples of Y radicals include substituted and unsubstituted alkylene groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, or amide linkages therein. Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^7R^8R^9$ represents a silane functional group containing three substituents (R^{7-9}), one or all of which are capable of being displaced by (e.g., nucleophilic) substitution. For example, at least one of the R^7,R^8, and R^9 substituents are groups such as alkoxy, aryloxy or halogen and the substituting group comprises a group such as hydroxyl present on an silane hydrolysis or condensation product, or equivalent reactive functional group present on the substrate film surface. Representative $SiR^7R^8R^9$ silane substitution includes where R^7 is C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, or halogen, and R^8 and R^9 are independently selected from C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, C_1-C_{20} alkyl, C_6-C_{20} aryl, C_7-C_{30} aralkyl, C_7-C_{30} alkaryl, halogen, and hydrogen. In one embodiment, R^7 is preferably C_1-C_4 alkoxy, C_6-C_{10} aryloxy or halogen.

Example silanes include: acryloxypropyltrimethoxysilane (APTMS, $H_2C{=}CHCO_2(CH_2)_3Si(OCH_3)_3$), acryloxypropyltriethoxysilane, acryloxypropylmethyldimethoxysilane, methacryloxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, and methacryloxypropylmethyldimethoxysilane

The term "vinyl functional group" as used herein means $CH_2{=}CH$- with optional alkyl substituents. The vinyl group can be present in a silicon compound such as a disilazane of the formula $(R_3Si)_2NH$, where at least one R is a functional group represented by the vinyl group, $CH_2{=}CH$-. The remaining R groups can be vinyl, alkyl, or aryl groups. The vinyl functional group in the silicon compounds can also be present in a silicon compound such as a silane of the formula $X{-}Y{-}SiR^7R^8R^9$. While not being bound by theory, the vinyl group may be covalently grafted to the surface of the nanoparticles using the reaction of surface hydroxyls with silanes of the type $X{-}Y{-}SiR^7R^8R^9$, where X represents a vinyl $CH_2{=}CH_2$- functional group, and Y represents a divalent organic radical covalently bonded to the vinyl functional group and the silane functional group. Examples of Y radicals include substituted and unsubstituted alkylene groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, or amide linkages therein. Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^7R^8R^9$ represents a silane functional group containing three substituents (R^7, R^8, and R^9). Examples of silanes include vinyltrimethoxysilane and vinyltriisopropoxysilane. Silazanes such as divinyltetramethyldisilazane ($H_2C{=}CH$- $Si(CH_3)_2NHSi(CH_3)_2$ $CH{=}CH_2$) can also be used. In some case, for example when silazanes are reacted in media containing alcohols, they can be transformed to the corresponding alkoxysilanes.

The inorganic particles can be surface functionalized by contacting the nanoparticles with the silane-containing reagents having the functional groups described above, in a solvent which will dissolve the silane. The contacting can be performed at room temperature or at elevated temperature, for example under reflux conditions. A magnesium fluoride colloid can be prepared using ethanol as the alcohol solvent. The silanes react with the residual –OH groups on the surface of the inorganic particles, thereby coupling the silanes to the surface of the inorganic particles. In this way, the nanoparticle surfaces are modified with a functional group.

The inorganic particles and the liquid medium of the electrolyte composition form a suspension. As used herein, the term “suspension” refers to a heterogeneous mixture in which solute-like particles eventually settle out of a solvent-like phase. In one embodiment, the inorganic particles eventually settle out of the liquid medium. In another embodiment, the suspension is a colloidal suspension, wherein the inorganic particles do not settle and cannot be separated out by ordinary filtering or centrifuging methods.

The suspension can be prepared by any suitable process. The inorganic particles can be mixed in a suitable carbonate or fluorinated solvent, as defined herein. The mixing can be done manually or using a mechanical, ultrasonic, or other type of mixer. The suspension can also be prepared by an in situ process in which the inorganic particles are precipitated in a compatible solvent that is suitable for use in the electrolyte composition. The suspension may also be formed by mixing the inorganic particles in a solvent that is displaced by a solvent or additive in a subsequent processing step. In this case, the electrolyte solvent containing the inorganic particles can be exchanged with a compatible solvent or additive that is suitable for use in the electrolyte composition. This exchange can be performed by several methods, including distillation, roto-vapping, freeze drying and re-dispersion, and spray drying and re-dispersion.

The electrolyte composition may further comprise a lithium boron compound. By “lithium boron compound” it is meant a compound having both lithium and boron in the empirical formula. The lithium and boron are not necessarily bonded directly to one another, but are present in the same compound.

Suitable lithium/boron compounds can include, for example, lithium terafluoroborate ($LiBF_4$), lithium difluoro(oxalato)borate [$LiBF_2(C_2O_4)$], lithium bis(oxalato)borate [$LiB(C_2O_4)_2$] also referred to as LiBOB, lithium bis(malonato)borate, lithium bis(2,2-dimethylmalonato)borate, lithium bis(methylmalonato)borate, lithium bis(ethylmalonato)borate, lithium bis(phenylmalonato)borate, lithium bis(ethylmethylmalonato)borate, lithium bis(allylmalonato)borate, lithium bis(glycolato)borate, lithium difluoro(glycolato)borate, and $Li_2B_{12}F_{12-x}H_x$, wherein x is 0 to 8, mixtures of lithium fluoride and anion receptors, such as $B(OC_6F_5)_3$. Combinations of the above lithium/boron compounds can also be used. In one embodiment, the lithium/boron compound comprises lithium tetrafluoroborate. In one embodiment, the lithium/boron compound comprises lithium difluoro(oxalato)borate. In one embodiment, the lithium/boron compound comprises lithium bis(oxalato)borate. Mixtures of two or more of these may also be used. The lithium/boron compounds disclosed herein may be obtained commercially or prepared using methods known in the art.

The electrolyte composition may further comprise an oxalate salt such as lithium tetrafluoro(oxalato)phosphate [$LiPF_4(C_2O_4)$], lithium difluorobis(oxalato)phosphate [$LiPF_2(C_2O_4)_2$], or lithium tris(oxalato)phosphate [$LiP(C_2O_4)_3$]. In one embodiment, the oxalate salt comprises lithium tetrafluoro(oxalato)phosphate. In one embodiment, the oxalate salt comprises lithium difluorobis(oxalato)phosphate. In one embodiment, the oxalate salt comprises lithium tris(oxalato)phosphate. Mixtures of two or more of these may also be used. The oxalate salts disclosed herein may be obtained commercially or prepared using methods known in the art.

In one embodiment, the electrolyte composition further comprises $LiB(C_2O_4)_2$, $LiBF_2(C_2O_4)$, $LiPF_4(C_2O_4)$, $LiPF_2(C_2O_4)_2$, $LiP(C_2O_4)_3$, or mixtures thereof.

The electrolyte composition can contain an amount of the lithium/boron compound and/or the oxalate salt in the range of from 0.1 percent by weight to about 10 percent by weight, based on the total weight of the electrolyte composition. In other embodiments, the lithium/boron compound and/or the oxalate salt can be present in the electrolyte composition in the range of about 0.01 to about 10 weight percent, or about 0.1 to about 5 weight percent, or about 0.5 weight percent to about 3 weight percent, or about 0.5 weight percent to about 2.5 weight percent, or about 0.5 weight percent to about 2 weight percent, of the total electrolyte composition.

In one embodiment, the electrolyte composition comprises 2,2-difluoroethyl acetate, ethylene carbonate, and magnesium fluoride particles. In another embodiment, the electrolyte composition comprises 2,2-difluoroethyl acetate, ethylene carbonate, fluoroethylene carbonate, and magnesium fluoride particles. In one embodiment, the electrolyte composition comprises 2,2-difluoroethyl acetate, ethylene carbonate, fluorethylene carbonate, propylene carbonate, and magnesium fluoride particles. In yet another embodiment, the electrolyte composition comprises 2,2-difluoroethyl acetate, propylene carbonate, and magnesium fluoride particles. In one embodiment, the electrolyte composition comprises about 10 weight percent to about 90 weight percent 2,2-difluoroethyl acetate, about 5 weight percent to about 40 weight percent carbonate, and about 0.01 weight percent to about 5 weight percent of inorganic particles, based on the total weight of the electrolyte composition.

In some embodiments, the electrolyte composition comprises about 5% to about 90%, or about 20% to about 80%, of 2,2-difluoroethyl acetate, and about 1% to about 65%, or about 5% to about 50%, of ethylene carbonate.

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

lithium hexafluorophosphate ($LiPF_6$),
lithium bis(trifluromethyl)tetrafluorophosphate ($LiPF_4(CF_3)_2$),
lithium bis(pentafluoroethyl)tetrafluorophosphate ($LiPF_4(C_2F_5)_2$),
lithium tris(pentafluoroethyl)trifluorophosphate ($LiPF_3(C_2F_5)_3$),
lithium bis(trifluoromethanesulfonyl)imide,
lithium bis(perfluoroethanesulfonyl)imide,

lithium (fluorosulfonyl) (nonafluorobutanesulfonyl)imide,
lithium bis(fluorosulfonyl)imide,
lithium perchlorate,
lithium hexafluoroarsenate,
lithium trifluoromethanesulfonate,
lithium tris(trifluoromethanesulfonyl)methide,
$Li_2B_{12}F_{12-x}H_x$ where x is equal to 0 to 8, and
mixtures of lithium fluoride and anion receptors such as $B(OC_6F_5)_3$.

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

Electrolyte compositions disclosed herein can additionally or optionally comprise additives that are known to those of ordinary skill in the art to be useful in conventional electrolyte compositions, particularly for use in lithium ion batteries. For example, electrolyte compositions disclosed herein can also include gas-reduction additives which are useful for reducing the amount of gas generated during charging and discharging of lithium ion batteries. Gas-reduction additives can be used in any effective amount, but can be included in an amount in the range of from about 0.05 weight percent to about 10 weight percent, alternatively from about 0.05 weight percent to about 5 weight percent of the electrolyte composition, or alternatively from about 0.5 weight percent to about 2 weight percent of the electrolyte composition.

Suitable gas-reduction additives that are known conventionally include, for example: halobenzenes such as fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, or haloalkylbenzenes; succinic anhydride; ethynyl sulfonyl benzene; 2-sulfobenzoic acid cyclic anhydride; divinyl sulfone; triphenylphosphate (TPP); diphenyl monobutyl phosphate (DMP); γ-butyrolactone; 2,3-dichloro-1,4-naphthoquinone; 1,2-naphthoquinone; 2,3-dibromo-1,4-naphthoquinone;

3-bromo-l ,2-naphthoquinone; 2-acetylfuran; 2-acetyl-5-methylfuran; 2-methyl imidazole1-(phenylsulfonyl)pyrrole; 2,3-benzofuran; fluoro-cyclotriphosphazenes such as 2,4,6-trifluoro-2-phenoxy-4,6-dipropoxy-cyclotriphosphazene and 2,4,6-trifluoro-2-(3-(trifluoromethyl)phenoxy)-6-ethoxy-cyclotriphosphazene; benzotriazole; perfluoroethylene carbonate; anisole; diethylphosphonate; fluoroalkyl-substituted dioxolanes such as 2-trifluoromethyldioxolane and 2,2-bistrifluoromethyl-1,3-dioxolane; trimethylene borate; dihydro-3-hydroxy-4,5,5-trimethyl-2(3H)-furanone; dihydro-2-methoxy-5,5-dimethyl-3(2H)-furanone; dihydro-5,5-dimethyl-2,3-furandione; propene sultone; diglycolic acid anhydride; di-2-propynyl oxalate; 4-hydroxy-3-pentenoic acid γ-lactone; $CF_3COOCH_2C(CH_3)(CH_2OCOCF_3)_2$; $CF_3COOCH_2CF_2CF_2CF_2CF_2CH_2OCOCF_3$; α-methylene-γ-butyrolactone; 3-methyl-2(5H)-furanone; 5,6-dihydro-2-pyranone; diethylene glycol, diacetate; triethylene glycol dimethacrylate; triglycol diacetate; 1,2-ethanedisulfonic anhydride; 1,3-propanedisulfonic anhydride; 2,2,7,7-tetraoxide 1,2,7-oxadithiepane; 3-methyl- 2,2,5,5-tetraoxide 1,2,5-oxadithiolane; hexamethoxycyclotriphosphazene; 4,5-dimethyl-4,5-difluoro-1,3-dioxolan-2-one; 2-ethoxy-2,4,4,6,6-pentafluoro-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine; 2,2,4,4,6-pentafluoro-2,2,4,4,6,6-hexahydro-6-methoxy-1,3,5,2,4,6-triazatriphosphorine ; 4,5-difluoro-1,3-dioxolan-2-one; 1,4-bis(ethenylsulfonyl)-butane; bis(vinylsulfonyl)-methane; 1,3-bis(ethenylsulfonyl)-propane; 1,2-bis(ethenylsulfonyl)-ethane; and 1,1’-[oxybis(methylenesulfonyl)]bis-ethene.

Other suitable additives that can be used are HF scavengers, such as silanes, silazanes (Si-NH-Si), epoxides, amines, aziridines (containing two carbons), salts of carbonic acid such as lithium oxalate, B_2O_5, and ZnO.

In another embodiment, there is a provided a method for forming the electrolyte composition. The method comprises:

combining:

a) a liquid medium comprising at least one non-aqueous solvent as defined herein;

b) inorganic particles comprising at least one Group 2 metal fluoride as described herein; and

c) at least one electrolyte salt, to form an electrolyte composition. The components can be combined in any suitable order. The step of combining can be accomplished by adding the individual components of the electrolyte composition sequentially or at the same time. In some embodiments, the components a) and b) are combined to make a suspension. After the formation of the suspension, an amount of the electrolyte salt is added to the suspension in order to produce the electrolyte composition having the desired concentration of the lithium salt. Typically, the electrolyte composition is agitated during and/or after the addition of the components in order to form a homogeneous mixture.

In another embodiment, there is provided herein an electrochemical cell comprising a housing, an anode and a 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 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 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, platinum, palladium, electroactive transition metal oxides comprising lithium or sodium, indium tin oxide, and conducting polymers such as polypyrrole and polyvinylferrocene.

During battery formation, at least a portion of the inorganic particles in the electrolyte composition form an SEI layer on one or both electrodes. In some embodiments, the active material on one or both electrodes of the electrochemical cell contains an SEI layer on at least a portion of the electrode surface. In another embodiment, the active material on one or both electrodes of the electrochemical cell contains an SEI layer on more than 50 percent, or more than 60 percent, or more than 70 percent, or more than 80 percent, or more than 90 percent, or more than 95 percent of the electrode surface. In an additional embodiment, the active material on one or both electrodes of the electrochemical cell contains an SEI layer on at least about 98 percent of the electrode surface. In one embodiment, at least one of the cathode or the anode has an SEI layer enriched in a Group 2 metal. In another embodiment, the cathode has an SEI layer enriched in a Group 2 metal. In yet another embodiment, the anode has an SEI layer enriched in a Group 2 metal. In a further embodiment, at least one of the cathode or the anode has an SEI layer enriched in a Group 2 metal, wherein the Group 2 metal is magnesium. On the anode, the SEI can suppress the reductive decomposition of the electrolyte; on the cathode electrode, the SEI can suppress the oxidation of the electrolyte components.

In another embodiment, the electrochemical cell is a lithium ion battery. Suitable cathode materials for a lithium ion battery include without limitation electroactive compounds comprising lithium and transition metals, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiCo_{0.2}Ni_{0.2}O_2$ or LiV_3O_8;

$Li_aCoG_bO_2$ ($0.90 \leq a \leq 1.8$, and $0.001 \leq b \leq 0.1$);

$Li_aNi_bMn_cCo_dR_eO_{2-f}Z_f$ where $0.8 \leq a \leq 1.2$, $0.1 \leq b \leq 0.9$, $0.0 \leq c \leq 0.7$, $0.05 \leq d \leq 0.4$, $0 \leq e \leq 0.2$, wherein the sum of b+c+d+e is about 1, and $0 \leq f \leq 0.08$;

$Li_aA_{1-b,}R_bD_2$ ($0.90 \leq a \leq 1.8$ and $0 \leq b \leq 0.5$);

$Li_aE_{1-b}R_bO_{2-c}D_c$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$ and $0 \leq c \leq 0.05$);

$Li_aNi_{1-b-c}Co_bR_cO_{2-d}Z_d$ where $0.9 \leq a \leq 1.8$, $0 \leq b \leq 0.4$, $0 \leq c \leq 0.05$, and $0 \leq d \leq 0.05$;

$Li_{1+z}Ni_{1-x-y}Co_xAl_yO_2$ where $0 < x < 0.3$, $0 < y < 0.1$, and $0 < z < 0.06$;

$LiNi_{0.5}Mn_{1.5}O_4$; $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, and $LiVPO_4F$.

In one embodiment, the electroactive compound includes $Li_aNi_bMn_cCo_dR_eO_{2-f}Z_f$ as defined above with the exceptions that $0.1 \leq b \leq 0.5$ and also $0.2 \leq c \leq 0.7$.

In the above chemical formulas A is Ni, Co, Mn, or a combination thereof; D is O, F, S, P, or a combination thereof; E is Co, Mn, or a combination thereof; G is Al, Cr, Mn, Fe, Mg, La, Ce, Sr, V, or a combination thereof; R is Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, Zr, Ti, a rare earth element, or a combination thereof; Z is F, S, P, or a combination thereof. Suitable cathodes and cathode active materials include those disclosed in U.S. Patent Nos. 5,962,166; 6,680,145; 6,964,828; 7,026,070; 7,078,128; 7,303,840; 7,381,496; 7,468,223; 7,541,114; 7,718,319; 7,981,544; 8,389,160; 8,394,534; and 8,535,832, and the references therein. By “rare earth element” is meant the lanthanide elements from La to Lu, and Y and Sc. In another embodiment the cathode material is an NMC cathode; that is, a LiNiMnCoO cathode. More specifically, cathodes in which the atomic ratio of Ni: Mn: Co is 1:1:1 ($Li_aNi_{1-b-c}Co_bR_cO_{2-d}Z_d$ where $0.98 \leq a \leq 1.05$, $0 \leq d \leq 0.05$, $b = 0.333$, $c = 0.333$, where R comprises Mn) or where the atomic ratio of Ni: Mn: Co is 5:3:2 ($Li_aNi_{1-b-c}Co_bR_cO_{2-d}Z_d$ where $0.98 \leq a \leq 1.05$, $0 \leq d \leq 0.05$, $c = 0.3$, $b = 0.2$, where R comprises Mn).

In another embodiment, the cathode in the lithium ion battery disclosed herein comprises a composite material of the formula $Li_aMn_bJ_cO_4Z_d$, wherein J is Ni, Co, Mn, Cr, Fe, Cu, V, Ti, Zr, Mo, B, Al, Ga, Si, Li, Mg, Ca, Sr, Zn, Sn, a rare earth element, or a combination thereof; Z is F, S, P, or a combination thereof; and $0.9 \leq a \leq 1.2$, $1.3 \leq b \leq 2.2$, $0 \leq c \leq 0.7$, $0 \leq d \leq 0.4$.

In another embodiment, the cathode in the lithium ion battery disclosed herein comprises a cathode active material exhibiting greater than 30 mAh/g capacity in the potential 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 $Li_xNi_yM_zMn_{2-y-z}O_{4-d}$, 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.

In another embodiment, the cathode in the lithium ion battery disclosed herein comprises a composite material represented by the structure of formula:

$$x(Li_{2-w}A_{1-v}Q_{w+v}O_{3-e}) \bullet (1-x)(Li_yMn_{2-z}M_zO_{4-d})$$

wherein:

x is about 0.005 to about 0.1;

A comprises one or more of Mn or Ti;

Q comprises one or more of Al, Ca, Co, Cr, Cu, Fe, Ga, Mg, Nb, Ni, Ti, V, Zn, Zr or Y;

e is 0 to about 0.3;

v is 0 to about 0.5.

w is 0 to about 0.6;

M comprises one or more of Al, Ca, Co, Cr, Cu, Fe, Ga, Li, Mg, Mn, Nb, Ni, Si, Ti, V, Zn, Zr or Y;

d is 0 to about 0.5;

y is about 0 to about 1; and

z is about 0.3 to about 1; and

wherein the $Li_yMn_{2-z}M_zO_{4-d}$ component has a spinel structure and the $Li_{2-w}Q_{w+v}A_{1-v}O_{3-e}$ component has a layered structure.

Alternatively, in another embodiment, in the Formula

$$x(Li_{2-w}A_{1-v}Q_{w+v}O_{3-e}) \bullet (1-x)(Li_yMn_{2-z}M_zO_{4-d})$$

x is about 0 to about 0.1, and all ranges for the other variables are as stated above.

In another embodiment, the cathode in the lithium ion battery disclosed herein comprises:

$$Li_aA_{1-x}R_xDO_{4-f}Z_f,$$

wherein:

A is Fe, Mn, Ni, Co, V, or a combination thereof;

R is Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, Zr, Ti, a rare earth element, or a combination thereof;

D is P, S, Si, or a combination thereof;

Z is F, Cl, S, or a combination thereof;

$0.8 \leq a \leq 2.2$;

$0 \leq x \leq 0.3$; and

$0 \leq f \leq 0.1$.

In another embodiment, the cathode in the lithium ion battery disclosed herein comprises a cathode active material which is charged to a potential greater than or equal to about 4.1 V, or greater than 4.35 V, or greater than 4.5 V, or greater than 4.6 V versus a Li/Li^+ reference electrode. Other examples are layered-layered high-capacity oxygen-release cathodes such as those described in U.S. Patent No. 7,468,223 charged to upper charging potentials above 4.5 V.

In yet another embodiment, the cathode comprises a) a cathode active material exhibiting greater than 30 mAh/g capacity in the potential range greater than 4.6 V versus a Li/Li^+ reference electrode; or b) a cathode active material which is charged to a potential greater than or equal to 4.35 V versus a Li/Li^+ reference electrode.

A cathode active material suitable for use herein can be prepared using methods such as, for example, 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 $LiOH \cdot H_2O$ at about 800°C to about 1000°C in oxygen for 3 to 24 hours. 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.

The cathode, in which the cathode active material is contained, can be prepared by mixing an effective amount of the cathode active material, for example about 70 percent by weight to about 97 percent by weight, with 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. The percentage by weight is based on the total weight of the cathode.

The electrochemical cell as disclosed herein further contains an anode, which comprises an anode active material that is capable of storing and releasing lithium ions. Examples of suitable anode active materials include, for example, lithium alloys such as lithium-aluminum alloy, lithium-lead alloy, lithium-silicon alloy, lithium-tin alloy; 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; nanocomposites containing antimony or tin, for example nanocomposites containing antimony, oxides of aluminum, titanium, or molybdenum, and carbon, such as those described by Yoon et al (*Chem. Mater.* 21, 3898-3904, 2009); and lithium titanates such as $Li_4Ti_5O_{12}$ and $LiTi_2O_4$. In one embodiment, the anode active material is lithium titanate or graphite. In another embodiment, the anode is graphite. In one embodiment, the anode comprises an anode active material and the anode active material is lithium titanate or graphite.

The 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, styrene-butadiene copolymer, or carboxymethyl cellulose is dissolved or dispersed in an organic solvent or water, which is then mixed with the anode 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 anode active material is bonded to the current collector. Suitable anode active materials and anodes are available commercially from companies such as Hitachi Chemical (Ibaraki, Japan), NEI Inc. (Somerset, NJ), and Farasis Energy Inc. (Hayward, CA).

The electrochemical cell further comprises a porous separator between the anode and the 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, polyimide, or a combination thereof. The pore size of the porous separator is sufficiently large to permit transport of ions to provide an 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. Patent Application Publication No. 2012/0149852, now U.S. Patent No. 8,518,525.

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 electrolyte compositions disclosed herein are useful in many types of electrochemical cells and batteries such as capacitors, nonaqueous batteries such as lithium batteries, flow batteries, and fuel cells.

The electrochemical cells and lithium ion battery disclosed herein may be used for grid storage or as a power source in various electronically-powered or -assisted devices (“electronic device”) such as a computer, a camera, a radio or a power tool, various telecommunications devices, or various transportation devices (including a motor vehicle, automobile, truck, bus or airplane).

EXAMPLES

The concepts disclosed herein are illustrated in the following examples. From the above discussion and these examples, one skilled in the art can ascertain the essential characteristics of the concepts disclosed herein, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt to various uses and conditions.

The meaning of abbreviations used is as follows: "°C" means degrees Celsius; "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); "s" means second(s); "psi" means pounds per square inch; "kPa" means kiloPascal(s); "A" means amperes; "mA" mean milliampere(s); "mAh/g" mean milliamperes hour(s) per gram; "V" means volt(s); "rpm" means revolutions per minute; "NMR" means nuclear magnetic resonance spectroscopy; "GC/MS" means gas chromatography/mass spectrometry; "Ex" means Example, and "Comp Ex" means Comparative Example.

Materials and Methods

Representative Preparation of 2,2-Difluoroethyl Acetate (DFEA)

The 2,2-difluoroethyl acetate used in the following Examples was prepared by reacting potassium acetate with HCF_2CH_2Br. The following is a typical procedure used for the preparation.

Potassium acetate (Aldrich, Milwaukee, WI, 99%) was dried at 100 ^oC 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 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 additional funnel.

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 of the reaction medium was brought to about 100 ^oC.

HCF_2CH_2Br (290 g, 2 mol, E.I. du Pont de Nemours and Co., 99%) was placed in the addition funnel and was slowly added to the reaction medium. The addition was mildly exothermic and the temperature of the reaction medium rose to 120-130 °C in 15-20 min after the start of the addition. The addition of HCF_2CH_2Br was kept at a rate which maintained the internal temperature at 125-135 °C. The addition took about 2-3 h. The reaction medium 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 medium 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 medium 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 $HCF_2CH_2OC(O)CH_3$ of about 98-98.5% purity, which was contaminated by a small amount of HCF_2CH_2Br (about 0.1-0.2%), HCF_2CH_2OH (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 µm, 0.25 µm; carrier gas – He, flow rate 1 mL/min; temperature program: 40 °C, 4 min, temp. ramp 30 °C/min, 230 °C, 20 min). Typically, the distillation of 240 g of crude product gave about 120 g of $HCF_2CH_2OC(O)CH_3$ of 99.89% purity, (250-300 ppm H_2O) 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 molecular sieves, until water was not detectable by Karl Fischer titration (i.e., <1 ppm).

Purification of Lithium bis(oxalato)borate

In a nitrogen purged dry box, lithium bis(oxalato)borate (LiBOB, Sigma-Aldrich, Milwaukee, WI) was purified by the following procedure. 25g of LiBOB was added to a 500 mL Erlenmeyer flask with 125 mL anhydrous acetonitrile. The mixture was stirred and heated to 40 °C for about 20 minutes. The warm mixture was filtered through a Buchner filter funnel with fine frit, and the filtrate was transferred into a 500 mL round bottom flask and allowed to cool to room temperature. A clear solution was obtained. To this clear solution, about 125 mL of cold anhydrous toluene (-20 °C) was added. This was stirred for an additional 20 minutes to form a precipitate. The mixture was filtered through a Buchner filter funnel with fine frit, and the filter cake was washed again with cold anhydrous toluene. The filter cake solid was placed in a flask and dried with stirring at room temperature overnight under high vacuum (100 mTorr), followed by further drying with stirring at 130 °C for 3 days under high vacuum (60 mTorr).

Cathode Preparation

The cathode electrodes used in the Examples and Comparative Examples herein were prepared by the following procedure.

Preparation of primer on aluminum foil current collector – using a polyimide/carbon composite

To prepare the polyamic acid, a prepolymer was first prepared. 20.6 wt % of PMDA:ODA prepolymer was prepared using a stoichiometry of 0.98:1 PMDA/ODA (pyromellitic dianhydride //ODA (4,4'-diaminodiphenyl ether) prepolymer). This was prepared by dissolving ODA in N-methylpyrrolidone (NMP) over the course of approximately 45 minutes at room temperature with gentle agitation. PMDA powder was slowly added (in small aliquots) to the mixture to control any temperature rise in the solution; the addition of the PMDA was performed over approximately two hours. The addition and agitation of the resulting solution under controlled temperature conditions. The final concentration of the polyamic acid was 20.6 wt % and the molar ratio of the anhydride to the amine component was approximately 0.98:1.

In a separate container, a 6 wt% solution of pyromellitic anhydride (PMDA) was prepared by combining 1.00 g of PMDA (Aldrich 412287, Allentown, PA) and 15.67 g of NMP (N-methylpyrrolidone). 4.0 grams of the PMDA solution was slowly added to the prepolymer and the viscosity was increased to approximately 90,000 poise (as measured by a Brookfield viscometer - # 6 spindle). This resulted in a finished prepolymer solution in which the calculated final PMDA:ODA ratio was 1.01:1.

5.196 Grams of the finished prepolymer was then diluted with 15.09 grams of NMP to create a 5 wt% solution. In a vial, 16.2342 grams of the diluted finished prepolymer solution was added to 0.1838 grams of TimCal Super C-65 carbon black. This was further diluted with 9.561 grams of NMP for a final solids content of 3.4 wt%, with a 2.72 prepolymer: carbon ratio. A Paasche VL# 3 Airbrush sprayer (Paasche Airbrush Company, Chicago, IL) was used to spray this material onto the aluminum foil (25 µm thick, 1145-0, Allfoils, Brooklyn Heights, OH). The foil was weighed prior to spraying to identify the necessary coating to reach a desired density of 0.06 mg/cm^2. The foil was then smoothed onto a glass plate, and sprayed by hand with the airbrush until coated. The foil was then dried at 125°C on a hot plate, and measured to ensure that the desired density was reached. The foil was found to be coated with 0.06 mg/cm^2 of the polyamic acid. Once the foil was dried and at the desired coating, the foil was imidized at 400 °C following the imidization procedure below

40°C to 125°C (ramp at 4°C/min)
125°C to 125°C (soak 30 min)
125°C to 250°C (ramp at 4°C/min)
250°C to 250°C (soak 30 min)
250°C to 400°C (ramp at 5°C/min)
400°C to 400°C (soak 20 min)

Coating of the cathode electroactive layer onto the primed Al foil

Preparation of the paste

The binder used was a Solef® 5130 (Solvay, Houston, TX) binder that was diluted to a 5.5% solution in NMP (*N*-methylpyrrolidone, Sigma Aldrich, St. Louis, MO). The following materials were used to make an electrode paste: 6.0352 g Farasis 1,1,1 NMC (Ni, Mn, Co, Farasis Energy, Hayward, CA) cathode active powder; 0.3342 g carbon black (Denka uncompressed, DENKA Corp., Japan); 6.0971 g PVDF (polyvinylidene difluoride (Solef® 5130) diluted with 2.1491 g NMP (portion 1) + 0.3858 g NMP (portion 2) (Sigma Aldrich). The materials were combined in a ratio of 90:5:5, cathode active powder: PVDF : carbon black, as described below. The final paste contained 44.7wt% solids.

The carbon black, the first portion of NMP, and the PVDF solution were first combined in a plastic THINKy container and centrifugally mixed (ARE-310, Thinky USA, Inc., Laguna Hills, CA) for 2 minutes at 2000 rpm. The cathode active powder and the second portion of NMP were added and the paste was centrifugally mixed once again at 2000 rpm for 2 minutes. An ultrasonic horn was immersed into the paste and ultrasonic energy was applied for approximately three seconds.

The aluminum foil (25 µm thick, 1145-0, Allfoils, Brooklyn Heights, OH) was pretreated with a polyimide/carbon primer as described in the procedure above.

Coating and Calendering the Cathode Electrode

The paste was manually cast using doctor blades with a 5 mil gate height plus 2 mil of Kapton® tape to produce a total gate opening of 7 mils onto the primed aluminum foil. The electrodes were dried for 60 minutes at 90 °C in a vacuum oven. The resulting 51-mm wide cathodes were placed between 125 mm thick brass sheets and passed through a calendar three times using 100 mm diameter steel rolls at 125°C with pressure increasing in each pass, at pressures of 18 psi, 24 psi, and 30 psi. The calendar is set to have a nip force (in lb) = 37.8 X regulator pressure (psi). Loadings of cathode active material were approximately 6.45-7.09 mg/cm^2.

Preparation of the Anode Electrode

The following is a typical procedure used for the preparation of anodes as used in the Examples and Comparative Examples herein. An anode paste was prepared from the following materials: 5.00 g graphite (CPreme® G5, Conoco-Philips, Huston, TX); 0.2743 g carbon black (Super C65, Timcal, Westlake, OH); 3.06 g PVDF (13% in NMP. KFL #9130, Kureha America Corp.); 11.00 g 1-methyl-2-pyrrolidinone (NMP); and 0.0097 g oxalic acid. The materials were combined in a ratio of 88 : 0.17 : 7 : 4.83, graphite : oxalic acid : PVDF : carbon black, as described below. The final paste contained 29.4% solids.

Oxalic acid, carbon black, NMP, and PVDF solution were combined in a plastic vial. The materials were mixed for 60 s at 2000 rpm using a planetary centrifugal mixer. The mixing was repeated a second time. The graphite was then added. The resulting paste was centrifugally mixed two times. The vial was mounted in an ice bath and homogenized twice using a rotor-stator for 15 min each time at 6500 rpm and then twice more for 15 min at 9500 rpm. The point where the stator shaft entered the vial was wrapped with aluminum foil to minimize water vapor ingress to the vial. Between each of the four homogenization periods, the homogenizer was moved to another position in the paste vial. The paste was then centrifugally mixed three times.

The paste was cast using a doctor blade with a 230 µm gate height on to copper foil (CF-LBX-10, Fukuda, Kyoto, Japan) using the automatic coater. The electrodes were dried for 30 min at 95 °C in the mechanical convection oven. The resulting 51-mm wide anodes were placed between 125 µm thick brass sheets and passed through a calender three times using 100 mm diameter steel rolls at ambient temperature with nip forces increasing in each of the passes, starting at 260 kg with the final pass at 770 kg.

Coin Cell Fabrication

Circular anodes 14.3 mm diameter and cathodes 12.7 mm diameter were punched out from the electrode sheets described above, placed in a heater in the antechamber of a glove box (Vacuum Atmospheres, Hawthorne, CA, with HE-493 purifier), further dried under vacuum overnight at 90 °C, and brought into an argon-filled glove box. Nonaqueous electrolyte lithium-ion CR2032 coin cells were prepared for electrochemical evaluation using the electrolyte compositions described below. The coin cell parts (case, spacers, wave spring, gasket, and lid) and coin cell crimper were obtained from Hohsen Corp (Osaka, Japan). The separator was a Celgard 2500 (Celgard/Polypore International, Charlotte, NC).

Coin Cell Evaluations at 25 °C

The coin cells were cycled twice for formation using a commercial battery tester (Series 4000, Maccor, Tulsa, OK) at ambient temperature using constant current charging and discharging between voltage limits of 3.0 – 4.6 V at a current of 17.5 mA per gram of cathode active material, which is approximately a 0.1C rate. Following this procedure, the coin cells were cycled using constant current charging and discharging between voltage limits of 3.0 – 4.6 V at a current of 87.5 mA per gram of cathode active material, which is approximately a C/2 rate. During each charge step, the voltage was subsequently held at 4.6 V until the current tapered to C/20 (approximately 8.75 mA per gram of active cathode material).

EXAMPLE 1

An electrolyte composition containing 70 weight percent 2,2-difluoroethyl acetate and 30 weight percent ethylene carbonate, with 1.27 weight percent MgF_2 (based on the solvent weight) and 2 weight percent LiBOB (based on the solvent weight), was prepared as follows.

Preparation of MgF_2 colloid in water:

In a 100 mL container, 24.3711 grams of magnesium chloride hydrate (Aldrich #M2670-500g Lot# BCBM7703V) was combined with

40.07 g of deionized water. In a second container, 8.8810 g ammonium fluoride (Aldrich #338869-100g Lot# S43837V) was dissolved in 40.17 g of water. The second solution was added to the first solution and allowed to stir for vigorously for about four hours.

The material was then poured in a 11” (28 cm) length (approximately 45 mm flat width, MWCO 12-kD) of spectra/por dialysis membrane (VWR, Radnor, PA). 112.10 g of the material was loaded into the membrane which was then folded and clamped shut. The membrane containing the colloid was suspended in a 5 L beaker which was filled with deionized water (18. Megaohms resistance). The water in the 5 L beaker was changed several times over the course of about 24 days.

The conductivity of the water was monitored, and the exchanged halted when no further conductivity rise was measured in the exchange solution.

The material was then removed from the spectra/por dialysis membrane and residual chloride content was checked by ion chromotagraphy using a Dionex AS17-C Ion Chromatography (IC) column that employs positively charge end-groups attached to the surface of polystyrene/divinylbenzene resin. The difference in acid strength determines the retention time on the resin with stronger acids retaining on the resin longer than weak acids generating a separation. The reproducible gradient generates a reproducible separation that is compared to known standards (Dionex 7 Anion Standard – product number 057590) by peak area. The standard levels analyzed for chloride and nitrate were 10, 5 , 2 and 1 PPM in these analyses. The areas of the standards are plotted to generate a response (area per PPM) that is applied to the area peaks in the samples to generate a concentration. The concentration is corrected for the system blank, which is normally minimal, and the dilution factor, normally a 100 fold dilution, to calculate the concentration in the original sample and reported in micrograms per milliliter.

The final measurement value for Cl- ion was 5.3 ppm Cl by this method.

Particle size analysis of the aqueous MgF_2 colloidal suspension was performed. The samples were diluted with water, about 100μL into 4 mL, and were measured on a Brookhaven Instruments system consisting of BI9000 goniometer set at scattering angle 90 degrees with 633nm HeNe laser(Melles Griot 35mW). The software used was Brookhaven Instruments Particle Sizing which is a dynamic light scattering technique. The data in Table 1 below is shown as d10, d50 and d90 values for the particle size distribution. "D10" is the diameter at which 10% of a sample's volume (or mass, if the density of the particles is constant for all particles) is lower than the particle diameter; "D50" is the diameter at which 50% of a sample's volume is lower than the particle diameter, and "D90" is the diameter at which 90% of the sample's volume is lower than the particle diameter, assuming spherical particles. D50 is also known as the "volume median", and assuming the density of the particles is constant for all particles, is a mass median diameter.

Table 1. Particle Size Results for MgF_2 Colloid in Water

dX	(nm)
10	78.08
50	85.07
90	190.19

Preparation of MgF_2 colloid in ethylene carbonate:

10 g of the 3.65 wt % MgF_2 colloid in water was combined with 10 g ethylene carbonate (EC, BASF, Independence, OH). Water was removed by placing this mixture with ethylene carbonate in a rotary evaporator. The material was placed under vacuum in the rotary evaporator at a set point temperature of 90 °C for approximately 90 minutes. The flask was placed under partial vacuum during this procedure. After no more water removal was observed, the hot water bath was turned off and allowed to return to ambient temperature. The material was allowed to rotate under vacuum during the cooling procedure for approximately 16 hours. This yielded 3.65 weight percent MgF_2 in ethylene carbonate.

Addition of 2,2-difluoroethyl acetate and $LiPF_6$ to the MgF_2 colloid in ethylene carbonate:

A portion (3.6588 g) of the 3.65 weight percent MgF_2 in ethylene carbonate mixture was combined with 8.8130g of 2,2-difluoroethyl acetate to form a mixture consisting of 70/30 2,2-difluoroethylacetate/ethylene carbonate on a weight basis.

The mixture containing the solvents and the MgF_2 was placed over molecular sieves (3A) and dried to less than 4 ppm water. At least two drying cycles were required to ensure that the water content was < 4 ppm. During this process, some of the magnesium fluoride precipitated from the formulation. The final MgF_2 content was determined by gravimetry by heating a small sample to 300 °C in air in a furnace; the MgF_2 content was determined to be 1.274 weight percent.

After isolation from the molecular sieves by pipet, 5.6999 g of dried material was recovered. 0.7329 g of $LiPF_6$ (lithium hexafluorophosphate, BASF, Independence, OH) was added to create a 1 M solution of $LiPF_6$. 1.9612 g of this mixture was combined with 0.04070 g of purified LiBOB to prepare the electrolyte composition of Example 1.

In the coin cells prepared with this electrolyte composition, the loading of the active component was 7.02-7.45 mg/cm^2 for the cathode, 4.39-4.66 mg/cm^2 for the anode. Results are presented in Table 2.

EXAMPLE 2

An electrolyte composition containing 70 weight percent 2,2-difluoroethyl acetate and 30 weight percent ethylene carbonate, with 2 weight percent MgF_2 (based on the solvent weight) and 2 weight percent LiBOB (based on the solvent weight), was prepared according to the procedure of Example 1, except with the following differences.

Preparation of MgF_2 colloid in water:

In a 100 mL container, 24.3711 grams of magnesium chloride hydrate (Aldrich M2670-500g) was combined with 40.07 g of deionized water. In a second container, 8.8810 g ammonium fluoride (Aldrich #338869100g) was dissolved in 40.17 g of water. The second solution was added to the first solution and allowed to stir for vigorously for about four hours.

The material was then poured in a 11" (28 cm) length (approximately 45 mm flat width, MWCO 12-kD) of spectra/por dialysis membrane (VWR, Radnor, PA). 112.10 g of the material was loaded into the membrane which was then folded and clamped shut. The membrane, containing the colloid, was suspended in a 5 liter beaker which was filled with dionized water (18. Megaohms resistance). The water in the 5 liter beaker was changed several times over the course of about 24 days.

The conductivity of the water was monitored, and the exchanged halted when no further conductivity rise was measured in the exchange solution.

The material was then removed from the spectra/por dialysis membrane and residual chloride content was checked by ion chromatography. The final measurement value for Cl^- ion was 5.3 ppm Cl by this method.

Preparation of MgF_2 colloid in ethylene carbonate:

40 g of the 3.65 wt % MgF_2 colloid in water was combined with 20 g ethylene carbonate (EC, BASF, Independence, OH). Water was removed by placing this mixture with ethylene carbonate in a rotary evaporator. The material was placed under vacuum in the rotary evaporator at a set point temperature of 90 ^{o}C for approximately 90 minutes. The flask was placed under partial vacuum during this procedure. After no more water removal was observed the hot water bath was turned off and allowed to return to ambient temperature. The material was allowed to rotate under vacuum during the cooling process, over the course of approximately 16 hours. This yielded 6.8 weight percent MgF_2 in ethylene carbonate.

Addition of 2,2-difluoroethyl acetate and $LiPF_6$ to the MgF_2 colloid in ethylene carbonate:

A portion (5.6791 g) of the 6.8 weight percent MgF_2 in ethylene carbonate mixture was combined with 12.2841 g of 2,2-difluoroethyl acetate to form a mixture consisting of 70/30 2,2-difluoroethylacetate/ethylene carbonate on a weight basis.

The mixture containing the solvents and the MgF_2 was placed over molecular sieves (3A) and dried to less than 4 ppm water. At least two drying cycles were required to ensure that the water content was < 4 ppm in the formulation. During this process, some of the magnesium fluoride precipitated from the formulation. The final MgF_2 content was determined by gravimetry by heating a small sample to 300 °C in air in a furnace; the MgF_2 content was determined to be 2.3 weight percent.

5.5411 g of material was isolated from the sieves by pipet after the drying process. 0.7045 g of $LiPF_6$ (BASF, Independence, OH) was added to create a 1 M solution of $LiPF_6$.

1.9621 g of this mixture was combined with 0.0414 g of purified LiBOB to prepare the electrolyte composition of Example 2.

In the coin cells prepared with this electrolyte composition, the loading of the active component was 7.02-7.45 mg/cm^2 for the cathode, 4.39-4.66 mg/cm^2 for the anode. Results are presented in Table 2.

EXAMPLE 3

An electrolyte composition containing 70 weight percent 2,2-difluoroethyl acetate and 30 weight percent ethylene carbonate, with 2 weight percent MgF_2 (based on the solvent weight) and 2 weight percent LiBOB (based on the solvent weight), was prepared according to the procedure of Example 2, except with the following differences.

2.4516 g of the mixture containing magnesium fluoride, 2,2 difluoroethyl acetate, ethylene carbonate, and 1M $LiPF_6$ was combined with 0.0507 of LiBOB to prepare the electrolyte composition. Results are presented in Table 2.

COMPARATIVE EXAMPLE A

An electrolyte composition containing 70 weight percent 2,2-

difluoroethyl acetate and 30 weight percent ethylene carbonate, with 2 weight percent LiBOB (based on the solvent weight), was prepared according to the procedure of Example 1, except that no colloidal MgF_2 was added.

The electrolyte formulation was prepared by combining 70 weight percent of 2,2-difluoroethyl acetate and 30 weight percent ethylene carbonate (EC, BASF, Independence, OH) in a nitrogen purged drybox. Molecular sieves (3A) were added and the mixture was dried to less than 1 ppm water. After filtration with a 0.25 micron PTFE syringe filter, $LiPF_6$ (BASF, Independence, OH) was added to make the formulation 1 M in $LiPF_6$.

3.2951 g of this solution was combined with 0.0800 grams of purified LiBOB to prepare the electrolyte composition of Comparative Example A.

In the coin cells prepared with this electrolyte composition, the loading of the active component was 6.59-7.16 mg/cm^2 for the cathode, 4.44-4.50 mg/cm^2 for the anode. Results are presented in Table 2.

Table 2. Cycle Life Durability Using NMC 111:C Cells at 25 °C

Example	Electrolyte Composition[1,2]	Coin Cell	T80 Cycle Life 80% [3]	Average Cycle Life 80%
Comp. Ex. A	70 wt% DFEA, 30 wt% EC + 2 wt% LiBOB	A-1	250	277
		A-2	278	
		A-3	122	
		A-4	305	
		A-5	253	
		A-6	304	
		A-7	424	
1	70 wt% DFEA, 30 wt% EC + 2 wt% LiBOB + 1.27 wt% MgF_2	1-1	373 *	328
		1-2	284	
2	70 wt% DFEA, 30 wt% EC + 2 wt% LiBOB + 2 wt% MgF_2	2-1	322	336
		2-2	430	
		2-3	255	
3	70 wt% DFEA, 30 wt% EC + 2 wt% LiBOB + 2 wt% MgF_2	3 -1	452	452

Notes:

[1] All compositions also contained $LiPF_6$ at 1M concentration in the solvent blend

[2] Weight percent values of MgF_2 based on total weight of solvents

[3] T80 Cycle Life 80% is the number of cycles needed to reach 80% of the maximum discharge capacity achieved during cycling at 25 °C

* This value projected from data at 290 cycles

EXAMPLE 4

In this Example, a cathode and anode were analyzed by X-ray Photoelectron Spectroscopy (XPS) after the coin cell evaluation to determine if the MgF_2 nanoparticles of the electrolyte composition were incorporated into the SEI layers on one or both of the electrodes, as evidenced by increased inorganic content and/or fluorine content on either or both the cathode and anode surfaces.

The electrodes were obtained from the coin cell of Example 3 after cycling as described herein above. After disassembly of the electrodes in an inert atmosphere dry box containing argon, the electrodes were gently rinsed twice with dimethyl carbonate. The electrodes were dried under the vacuum of the antichamber for approximately 10 hours at room temperature..

XPS surface and depth profile analyses were performed with a Physical Electronics Quantum/Quantera Scanning XPS Microprobe, using a monochromatic Al X-ray (1486.6 eV) beam operated at 20 kV and 100 W. The X-ray beam was generated using an electron gun and scanned over ~1400 µm×~200 µm to define the analytical area. The take-off angle was 45° relative to the sample normal. Depth profiles were performed using 2 KeV Ar^+ ions with 4 mm×4 mm raster size. The calibrated SiO_2 sputter rate under this sputter condition was at ~2.5nm/min. PHI MultiPak@ software version 9.0 was used for data analysis.

The XPS results from the anode and cathode surfaces are listed in Table 3. Based on the reported binding energies in the literature for Mg1s and Mg2p peaks, Mg assigned as MgF_2, i.e., from the MgF_2 nanoparticles in the electrolyte composition, was detected on the cathode surface. Mg was not detected at the outermost anode surface, but XPS depth profile study showed that low levels of Mg were present at the anode sub-surfaces.

Table 3. Surface Concentrations of Elements Detected by XPS on the Anode and Cathode (in Atom%)

	Li	B	C	N	O	F	Mg	P	Si	Mn	Co	Ni
Anode	28.1	0.8	28.7	0.2	26.6	14.2	ND	0.9	ND	ND	0.1	0.3
Cathode	3.3	0.7	44.7	0.6	24.1	20.1	0.7	1.3	3.3	0.2	0.5	0.5

Notes:

The concentrations reported in Table 3 are normalized to 100%.

H and He cannot be detected by XPS.

ND = not detected by XPS with detection limit at ~0.1 atom%.

The XPS depth profile results from the electrodes are shown in Figure 1 and Figure 2. Based on the depth profile data, various levels of Mg were detected from both the anode and cathode after sputtering. This implied the incorporation of MgF_2 nanoparticles into the electrode SEI layers. On the anode surface, Mg was not detected at zero depth prior to sputtering. After initial sputtering, a trace level of Mg was detected and slowly increased into the anode sub-surfaces. On the cathode side, Mg was detected at zero depth and more Mg was present into sub-surfaces compared to the anode side.

The presence of magnesium cations on both interfaces demonstrates that the electrolyte compositions containing MgF_2 modify the surfaces of the electrode interfaces. Without being bound to any theory, it is believed that this modification changes the nature and the interaction of the electrolyte with those interfaces, thereby improving the electrochemical peformance of the cells.

EXAMPLE 5

An electrolyte composition containing 70 weight percent 2,2-difluoroethyl acetate and 30 weight percent ethylene carbonate, with 3.1 weight percent MgF_2 (based on the solvent weight) and 2 weight percent LiBOB (based on the solvent weight), was prepared according to the procedure of Example 1, except with the following differences.

Preparation of MgF_2 colloid in water:

In a 100 mL container, 24.3711 grams of magnesium chloride hydrate (Aldrich M2670-500g) was combined with 40.07 g of deionized water. In a second container, 8.8810 g ammonium fluoride (Aldrich #338869100g) was dissolved in 40.17 g of water. The second solution was added to the first solution and allowed to stir for vigorously for about four hours.

The material was then poured in a 11” (28 cm) length (approximately 45 mm flat width, MWCO 12-kD) of spectra/por dialysis membrane (VWR, Radnor, PA). 112.10 g of the material was loaded into the membrane which was then folded and clamped shut. The membrane, containing the colloid, was suspended in a 5 liter beaker which was filled with dionized water (18. Megaohms resistance). The water in the 5 liter beaker was changed several times over the course of about 24 days.

The conductivity of the water was monitored, and the exchanged halted when no further conductivity rise was measured in the exchange solution.

The material was then removed from the spectra/por dialysis membrane and residual chloride content was checked by ion chromatography. The final measurement value for Cl- ion was 5.3 ppm Cl by this method.

Preparation of MgF_2 colloid in ethylene carbonate:

40g of the 3.65 wt % MgF_2 colloid in water was combined with 10 g ethylene carbonate (EC, BASF, Independence, OH). Water was removed by placing this mixture with ethylene carbonate in a rotary evaporator. The material was placed under vacuum in the rotary evaporator at a set point temperature of 90 ^{o}C for approximately 90 minutes. The flask was placed under partial vacuum during this procedure. After no more water removal was observed the hot water bath was turned off and allowed to return to ambient temperature. The material was allowed to rotate under vacuum during the cooling process, over the course of approximately 16 hours to produce 12.74 weight percent MgF_2 in ethylene carbonate.

Addition of 2,2-difluoroethyl acetate and $LiPF_6$ to the MgF_2 colloid in ethylene carbonate:

A portion (6.1485 g) of the 6.8 weight percent MgF_2 in ethylene carbonate mixture was combined with 12.2772 g of 2,2-difluoroethyl acetate to form a mixture consisting of a 70/30 2,2-difluoroethylacetate/ethylene carbonate on a weight basis.

The mixture containing the solvents and the MgF_2 was placed over molecular sieves (3A) and the mixture was dried to less than 4 ppm water. At least two drying cycles were required to ensure that the water content was < 4 ppm in the formulation. During this process, some of the magnesium fluoride precipitated from the formulation. The final MgF_2 content was determined by gravimetry by heating a small sample to 300 °C in air in a furnace; the MgF_2 content was determined to be 3.1 weight percent..

14.0944 g of material was isolated from the sieves by pipet after the drying process. 1.7422 g of $LiPF_6$ (BASF, Independence, OH) was added to create a 1 M solution of $LiPF_6$.

3.9221 g of this mixture was combined with 0.0807 g of purified LiBOB to prepare the electrolyte composition of Example 5.

In the coin cells prepared with this electrolyte composition, the loading of the active component was 6.6-6.9 mg/cm^2 for the cathode, 4.17-439 mg/cm^2 for the anode.

The cell was evaluated and cycled for 160 cycles. The coin cells were de-crimped inside of the Ar box. The electrodes were isolated from other cell parts and individually washed three times by gently submerging the electrodes in dried dimethyl carbonate. The washed electrodes were allowed to dry under vacuum at room temperature for approximately 18 hours. The cathode and anode were analyzed by XPS as described in Example 4.

The XPS results from the anode and cathode surfaces are listed in Table 4. Mg as MgF_2, i.e., from the MgF_2 nanoparticles in the electrolyte composition, was detected on both the anode and cathode surfaces. The electrodes were found to contain more Mg than the electrodes of Example 4 (where Mg was not detected at the outermost anode surface and low levels of Mg were present into the anode sub-surfaces). These results are consistent with the electrodes of Example 5 having been part of a coin cell cycled in an electrolyte composition containing 3.2 weight percent MgF_2 while the electrodes of Example 4 were part of a coin cell cycled in an electrolyte composition containing a 2 weight percent MgF_2, a lower amount.

Table 4. Surface Concentrations of Elements Detected by XPS on the Anode and Cathode (in Atom%)

	Li	B	C	N	O	F	Mg	Si	P	Co	Ni
Anode	23.3	0.7	23.7	0.2	17.4	31.0	0.8	1.3	1.6	<0.1	<0.1
Cathode	6.2	1.1	31.0	0.4	20.5	32.3	4.8	0.9	2.5	0.2	<0.1

Notes:

The concentrations reported in Table 4 are normalized to 100%.

H and He cannot be detected by XPS.

ND = not detected by XPS with detection limit at ~0.1 atom%.

The XPS depth profile results from the electrodes are shown in Figures 3 and 4. The presence of various levels of Mg from both the anode and cathode implies the incorporation of MgF_2 nanoparticles into the electrode SEI layers. In comparison with the electrodes cycled with 2wt% MgF_2 additive in Example 4, the electrodes cycled with 3.1wt% MgF_2 contained more Mg both at the zero depth (as-received outermost surfaces) as well as into sub-surfaces after sputtering.

These results demonstrate that increasing the level of MgF_2 in the electrolyte compositions (from 2.0 wt % to 3.1 wt %) increased the presence of magnesium cations at the electrode interfaces. There is a clear dependence of the extent of incorporation of magnesium with the amount of MgF_2 which is present in the electrolyte, at least up to about 3.1 wt %.

EXAMPLE 6

High-resolution transmission electron microscopy (TEM) along with elemental analysis via energy dispersive spectroscopy (EDS) were used to characterize the passivation layers (SEI) formed on the electrodes when MgF_2 was used as an additive in the electrolyte. Electrodes from Example 3 were analyzed as described below.

In order to minimize exposing the cycled anodes and cathodes to air and humidity, the sample preparation was kept to the least possible time from the argon-sealed vials to the vacuum of the microscope column. A reverse action pair of tweezers was used to hold a holey-carbon coated Cu TEM grid. The cycled electrode were removed from the vial and the electrode material was scraped using a single-edge razor blade onto the grid. The grid was placed on an FEI double-tilt ultra-twin sample holder and quickly transferred to the microscope column. The vial to the microscope column was typically achieved within a time interval of 5 minutes.

The microstructure of the scraped anode and cathode sample powders was analyzed by high-resolution transmission electron microscopy (TEM) and its associated elemental analysis by energy dispersive spectroscopy (EDS) using an FEI Tecnai F-20 scanning transmission electron microscope (STEM) equipped with a field-emitting electron source. The microscope was operated at an accelerating voltage of 200 kV. The elemental analysis was accomplished with an Oxford Instruments INCA x-sight EDS system attached to the microscope column and capable of identifying elements as light as boron. This particular EDS system had a Li-doped Si detector and an ATW ultra-thin window.

The STEM/EDS analysis indicates magnesium fluoride is present at the anode interface or SEI as well as on the cathode surfaces.

Figure 5 represents a bright-field transmission electron microscopy image of the anode interface of the SEI of Example 3.

Figure 6 shows the selected area electron diffraction pattern of the anode interface or the SEI of Example 3 corresponding to the anode interface region shown in Figure 5; the diffraction pattern (~ 100 nm^2) was identified as MgF_2. Figures 5 and 6 together show that the aggregates of nanocrystals on the anode surface are magnesium fluoride.

Figure 7 shows a high-angle annular dark field image of this SEI derived from the Example 3 evaluation. Energy dispersive spectroscopy (EDS) shown in Figure 8 identified that the elements magnesium and fluorine are present on the anode surfaces.

Figure 9 shows the area being measured in the EDS measurements (which are shown for regions 1 and 2 in Figures 10 and 11). Region 1 focuses on the carbon black + binder area in the cathode electrode and shows evidence of magnesium, but not in the more aggregated form present on the anode. Region 2 is on the surface of the NMC 111 active oxide, and also shows the presence of magnesium.

The presence of magnesium cations at both electrode interfaces demonstrates that the electrolyte compositions containing MgF_2 modify the surfaces of the electrode interfaces. In the case of the anode, electron diffraction clearly identifies the SEI as containing as magnesium fluoride. This modification of the electrode interfaces changes the nature and the interaction of the electrolyte with those interfaces, thereby improving the electrochemical peformance of the cells.

CLAIMS

What is claimed is:

1. An electrolyte composition comprising:
   a) a liquid medium comprising at least one non-aqueous solvent;
   b) inorganic particles comprising at least one Group 2 metal fluoride and having an average primary median particle diameter d_{50} in the range of about 1 nm to about 700 nm as determined by dynamic light scattering; and
   c) at least one electrolyte salt;

wherein the inorganic particles and the liquid medium form a suspension.

2. The electrolyte composition of claim 1, wherein the non-aqueous solvent comprises at least one fluorinated solvent.

3. The electrolyte composition of claim 2, wherein the fluorinated solvent is:

a) a fluorinated acyclic carboxylic acid ester represented by the formula:

$$R^1\text{-COO-}R^2,$$

b) a fluorinated acyclic carbonate represented by the formula:

$$R^3\text{-OCOO-}R^4,$$

c) a fluorinated acyclic ether represented by the formula:

$$R^5\text{-O-}R^6,$$

or mixtures thereof;

wherein

i) R^1 is H, an alkyl group, or a fluoroalkyl group;

ii) R^3 and R^5 is each independently a fluoroalkyl group and can be either the same as or different from each other;

iii) R^2, R^4, and R^6 is each independently an alkyl group or a fluoroalkyl group and can be either the same as or different from each other;

iv) either or both of R^1 and R^2 comprises fluorine; and

v) R^1 and R^2, R^3 and R^4, and R^5 and R^6, each taken as a pair, comprise at least two carbon atoms but not more than seven carbon atoms.

4. The electrolyte composition of claim 3, wherein R^1 and R^2, R^3 and R^4, and R^5 and R^6, each taken as a pair, further comprise at least two fluorine atoms, with the proviso that none of R^1, R^2, R^3, R^4, R^5, nor R^6 contains a FCH_2- group or a –FCH- group.

5. The electrolyte composition of claim 3, wherein the fluorinated solvent is a fluorinated acyclic carboxylic acid ester.

6. The electrolyte composition of claim 3, wherein the fluorinated acyclic carboxylic acid ester is CH_3-COO-CH_2CF_2H, CH_3CH_2-COO-CH_2CF_2H, F_2CHCH_2-COO-CH_3, F_2CHCH_2-COO-CH_2CH_3, CH_3-COO-$CH_2CH_2CF_2H$, CH_3CH_2-COO-$CH_2CH_2CF_2H$, $F_2CHCH_2CH_2$-COO-CH_2CH_3, CH_3-COO-CH_2CF_3, CH_3CH_2-COO-CH_2CF_2H, H-COO-CH_2CF_2H, H-COO-CH_2CF_3, or mixtures thereof.

7. The electrolyte composition of claim 2, wherein the fluorinated solvent comprises 2,2-difluoroethyl acetate or 2,2-difluoroethyl methyl carbonate.

8. The electrolyte composition of claim 1, wherein the non-aqueous solvent comprises at least one carbonate.

9. The electrolyte composition of claim 8, wherein the carbonate comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, vinylene carbonate, 4-fluoroethylene carbonate, or a mixture thereof.

10. The electrolyte composition of claim 1, wherein the suspension is a

colloidal suspension.

11. The electrolyte composition of claim 1, wherein the Group 2 metal fluoride is selected from the group consisting of MgF_2, CaF_2, SrF_2, BaF_2, and mixtures thereof.

12. The electrolyte composition of claim 11, wherein the Group 2 metal fluoride comprises MgF_2.

13. The electrolyte composition of claim 1, wherein the electrolyte composition comprises an amount of the inorganic particles in the range of about 0.01 weight percent to about 10 weight percent, based on the total weight of the electrolyte composition.

14. The electrolyte composition of claim 1, further comprising $LiB(C_2O_4)_2$, $LiBF_2(C_2O_4)$, $LiPF_4(C_2O_4)$, $LiPF_2(C_2O_4)_2$, $LiP(C_2O_4)_3$, or mixtures thereof.

15. The electrolyte composition of claim 1, wherein the electrolyte composition comprises about 10 weight percent to about 90 weight percent 2,2-difluoroethyl acetate, about 5 weight percent to about 40 weight percent carbonate, and about 0.01 weight percent to about 5 weight percent of the inorganic particles, based on the total weight of the electrolyte composition.

16. An electrochemical cell comprising:
(a) a housing;
(b) an anode and a cathode disposed in the housing and in ionically conductive contact with one another;
(c) the electrolyte composition of claim 1 disposed in the housing and providing an ionically conductive pathway between the anode and the cathode; and
(d) a porous separator between the anode and the cathode.

17. The electrochemical cell of Claim 16, wherein the electrochemical cell is a lithium ion battery.

18. The electrochemical cell of claim 17, wherein at least one of the cathode or the anode has an SEI layer enriched in a Group 2 metal.

19. The electrochemical cell of claim 18, wherein the Group 2 metal is magnesium.

20. The electrochemical cell of Claim 17, wherein the anode comprises an anode active material and the anode active material is lithium titanate or graphite.

21. The electrochemical cell of Claim 17, wherein the cathode comprises

a) a cathode active material exhibiting greater than 30 mAh/g capacity in the potential range greater than 4.6 V versus a Li/Li^+ reference electrode; or

b) a cathode active material which is charged to a potential greater than or equal to 4.35 V versus a Li/Li^+ reference electrode.

22. The electrochemical cell of claim 17, wherein the cathode comprises

$$Li_aMn_bJ_cO_4Z_d,$$

wherein:

J is Ni, Co, Mn, Cr, Fe, Cu, V, Ti, Zr, Mo, B, Al, Ga, Si, Li, Mg, Ca, Sr, Zn, Sn, a rare earth element, or a combination thereof;

Z is F, S, P, or a combination thereof; and

$0.9 \leq a \leq 1.2$, $1.3 \leq b \leq 2.2$, $0 \leq c \leq 0.7$, $0 \leq d \leq 0.4$.

23. The electrochemical cell of Claim 17, wherein the cathode active material comprises:

a) a lithium-containing manganese composite oxide having a spinel structure as active material, the lithium-containing manganese composite oxide comprising oxides of the formula

$$Li_xNi_yM_zMn_{2-y-z}O_{4-d}$$

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; or

b) a composite material represented by the formula:

$$x(Li_{2-w}A_{1-v}Q_{w+v}O_{3-e}) \bullet (1-x)(Li_yMn_{2-z}M_zO_{4-d})$$

wherein:

x is about 0 to about 0.1;

A comprises one or more of Mn or Ti;

Q comprises one or more of Al, Ca, Co, Cr, Cu, Fe, Ga, Mg, Nb, Ni, Ti, V, Zn, Zr or Y;

e is 0 to about 0.3;

v is 0 to about 0.5.

w is 0 to about 0.6;

M comprises one or more of Al, Ca, Co, Cr, Cu, Fe, Ga, Li, Mg, Mn, Nb, Ni, Si, Ti, V, Zn, Zr or Y;

d is 0 to about 0.5;

y is about 0 to about 1;

z is about 0.3 to about 1; and

wherein the $Li_yMn_{2-z}M_zO_{4-d}$ component has a spinel structure and the $Li_{2-w}Q_{w+v}A_{1-v}O_{3-e}$ component has a layered structure; or

c) a composition of the formula $Li_aNi_bMn_cCo_dR_eO_{2-f}Z_f$,

wherein:

R is Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, Zr, Ti, a rare earth element, or a combination thereof, and Z is F, S, P, or a combination thereof; and $0.8 \leq a \leq 1.2$, $0.1 \leq b \leq 0.9$, $0.0 \leq c \leq 0.7$, $0.05 \leq d \leq 0.4$, $0 \leq e \leq 0.2$; wherein the sum of b+c+d+e is about 1; and $0 \leq f \leq 0.08$; or

d) a composition of the formula $Li_aA_{1-x}R_xDO_{4-f}Z_f$,

wherein:

A is Fe, Mn, Ni, Co, V, or a combination thereof;

R is Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, Zr, Ti, a rare earth element, or a combination thereof;

D is P, S, Si, or a combination thereof;

Z is F, Cl, S, or a combination thereof ;

$0.8 \leq a \leq 2.2$;

$0 \leq x \leq 0.3$; and

$0 \leq f \leq 0.1$; or

e) a composition of the formula Li_aA_{1-b},R_bD_2,

wherein:

A is Ni, Co, Mn, or a combination thereof;

R is Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, Zr, Ti, a rare earth element, or a combination thereof;

D is O, F, S, P, or a combination thereof; and

$0.90 \leq a \leq 1.8$ and $0 \leq b \leq 0.5$.

24. An electronic device, transportation device, or telecommunications device, comprising an electrochemical cell according to Claim 16.

25. A method comprising:

combining:

a) a liquid medium comprising at least one non-aqueous solvent;

b) inorganic particles comprising at least one Group 2 metal fluoride and having an average primary median particle diameter d_{50} in the range of about 1 nm to about 500 nm as determined by dynamic light scattering; and

c) at least one electrolyte salt;

to form an electrolyte composition wherein the inorganic particles and the liquid medium form a suspension.

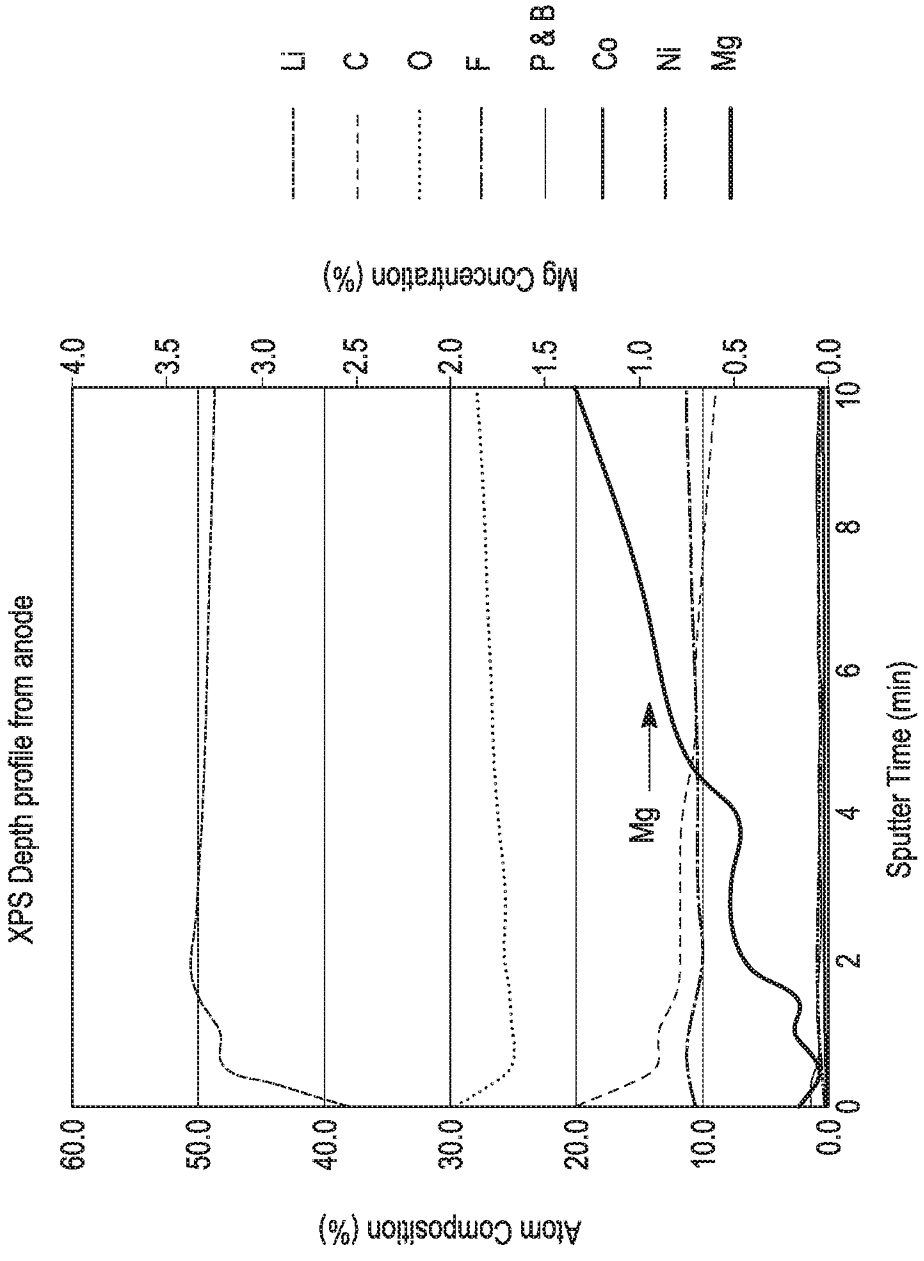

XPS Depth profile from anode
Atom Composition (%)
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Mg Concentration (%)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Sputter Time (min)
0
2
4
6
8
10
Mg
Li
C
O
F
P & B
Co
Ni
Mg

FIG. 1

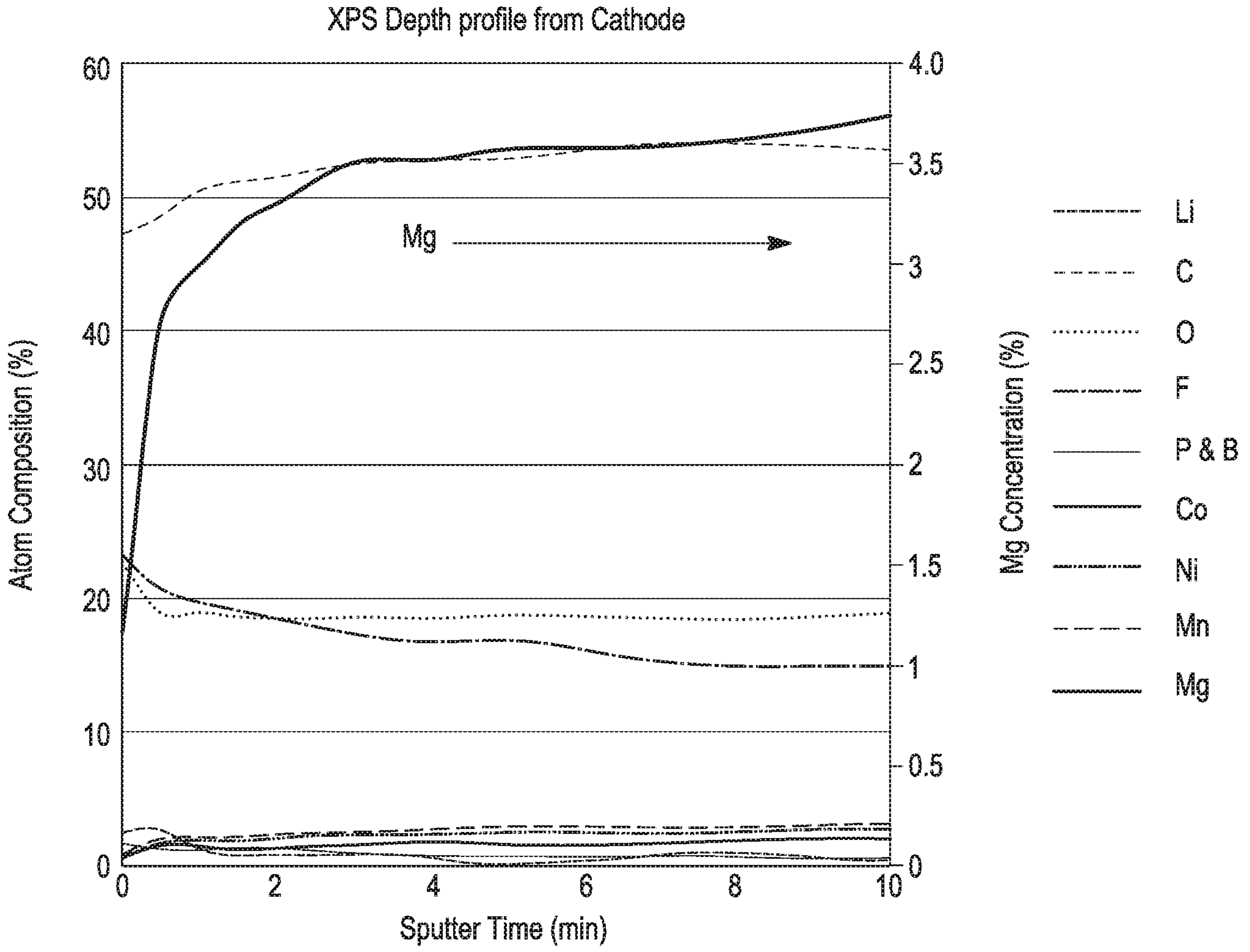

XPS Depth profile from Cathode
Atom Composition (%)
60
50
40
30
20
10
0
Sputter Time (min)
0
2
4
6
8
10
Mg Concentration (%)
4.0
3.5
3
2.5
2
1.5
1
0.5
0
Mg
Li
C
O
F
P & B
Co
Ni
Mn
Mg

FIG. 2

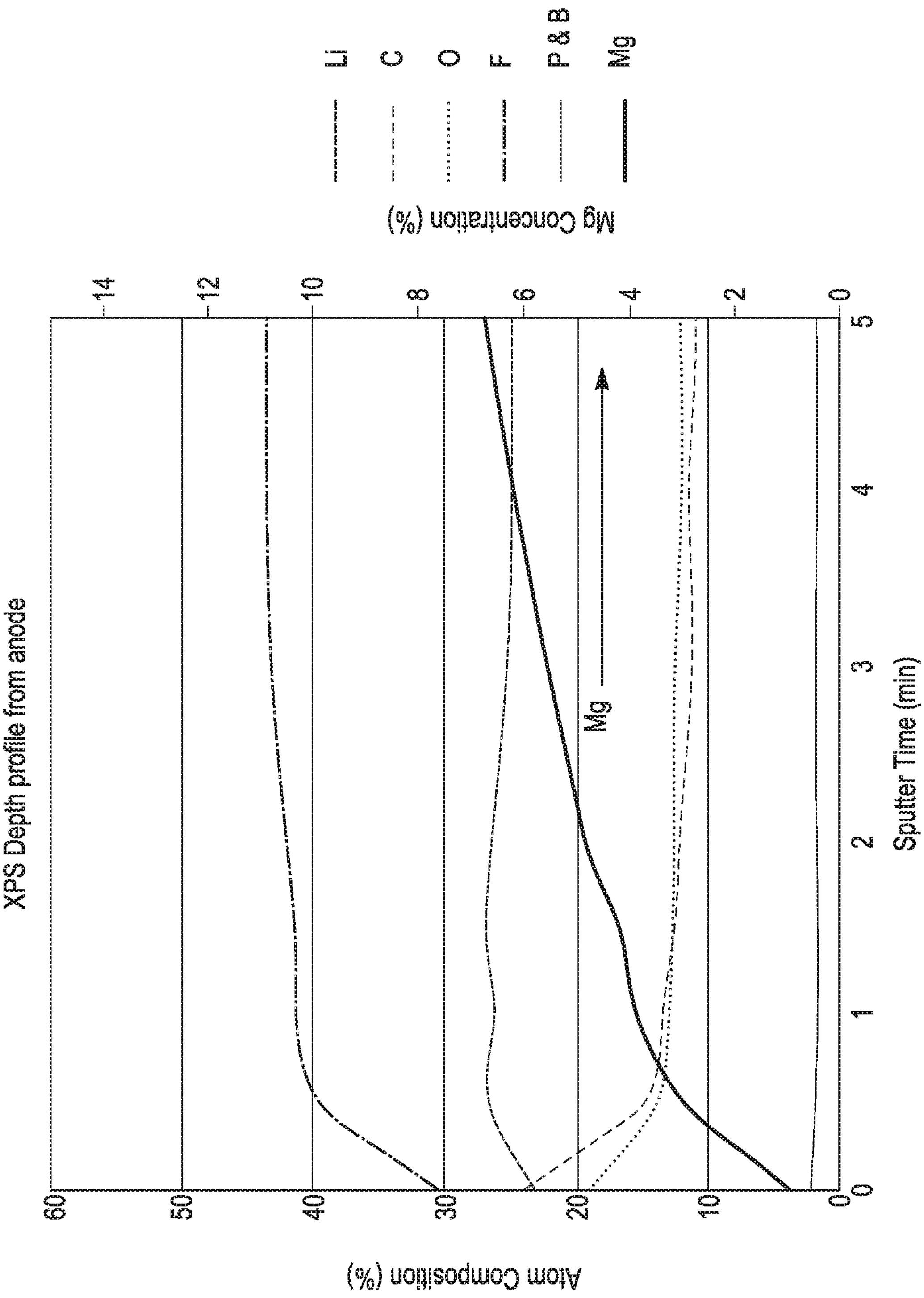

XPS Depth profile from anode
Atom Composition (%)
0
10
20
30
40
50
60
Mg Concentration (%)
0
2
4
6
8
10
12
14
Sputter Time (min)
0
1
2
3
4
5
Mg
Li
C
O
F
P & B
Mg

FIG. 3

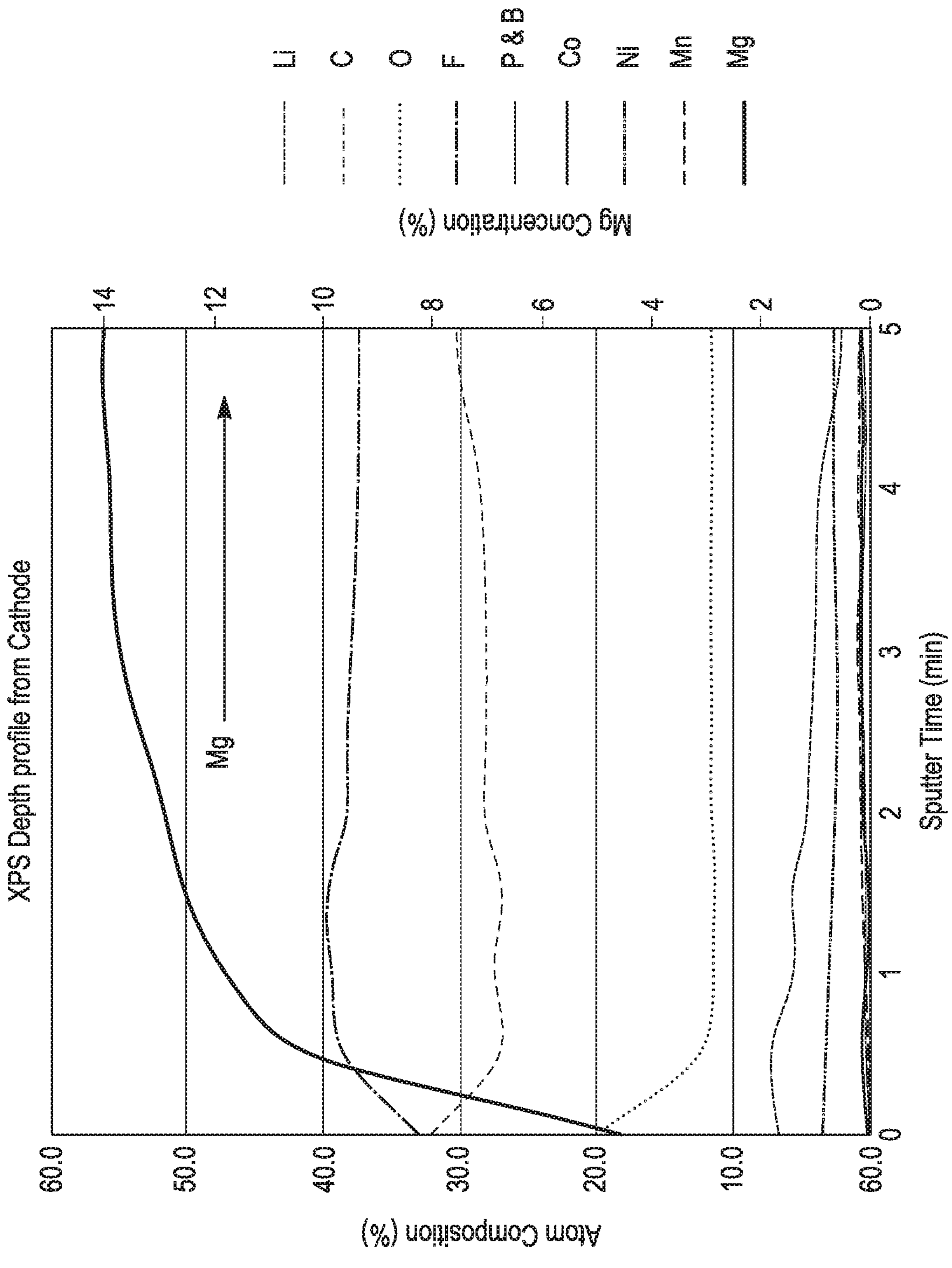

XPS Depth profile from Cathode
Atom Composition (%)
60.0
50.0
40.0
30.0
20.0
10.0
60.0
Mg Concentration (%)
14
12
10
8
6
4
2
0
Sputter Time (min)
0
1
2
3
4
5
Mg
Li
C
O
F
P & B
Co
Ni
Mn
Mg

FIG. 4

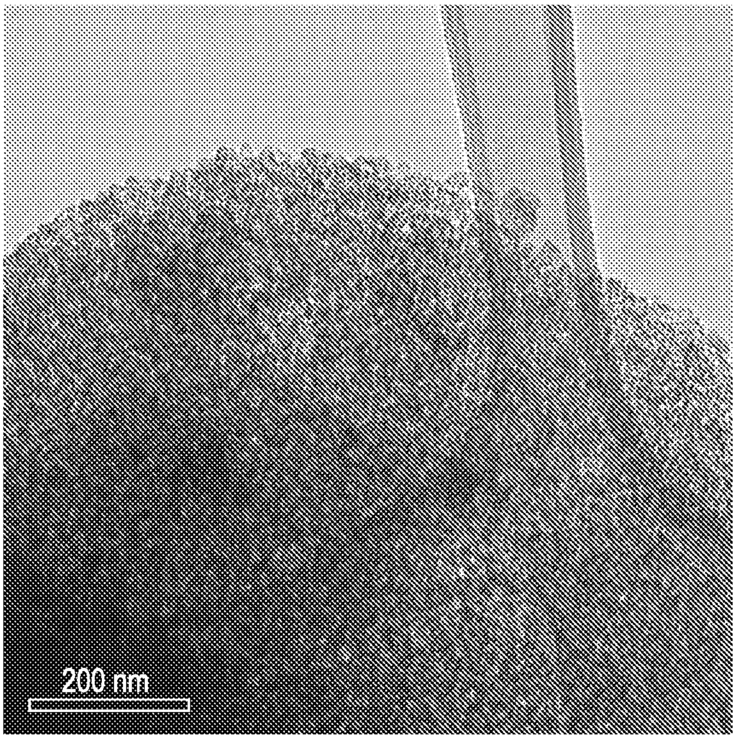


FIG. 5

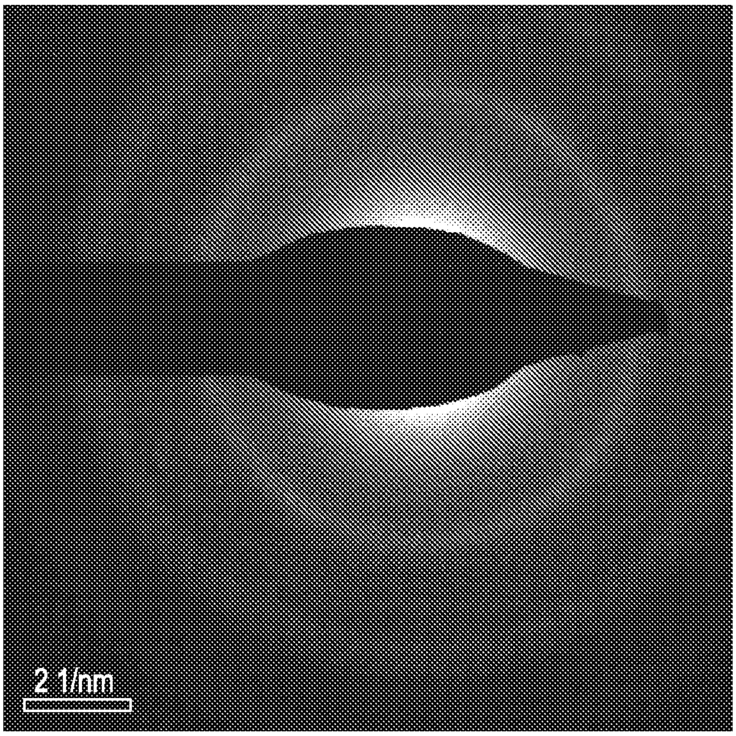


FIG. 6

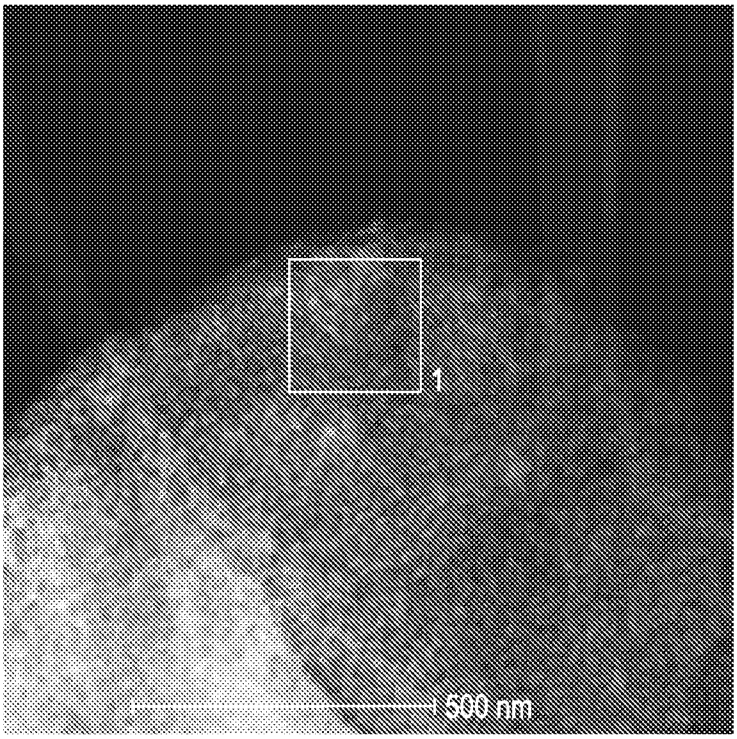


FIG. 7

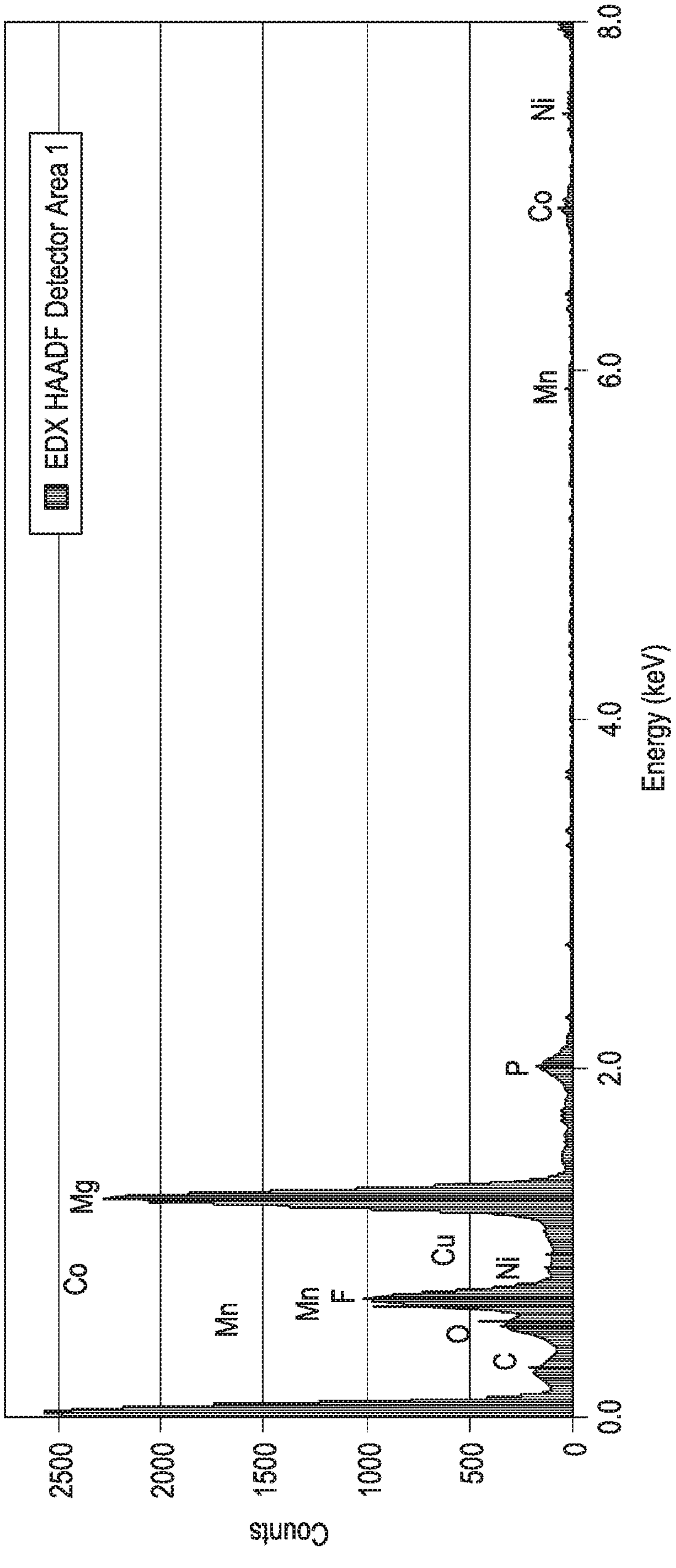

EDX HAADF Detector Area 1
Counts
2500
2000
1500
1000
500
0
0.0
2.0
4.0
6.0
8.0
Energy (keV)
C
O
Mn
F
Mn
Co
Ni
Cu
Mg
P
Mn
Co
Ni

FIG. 8

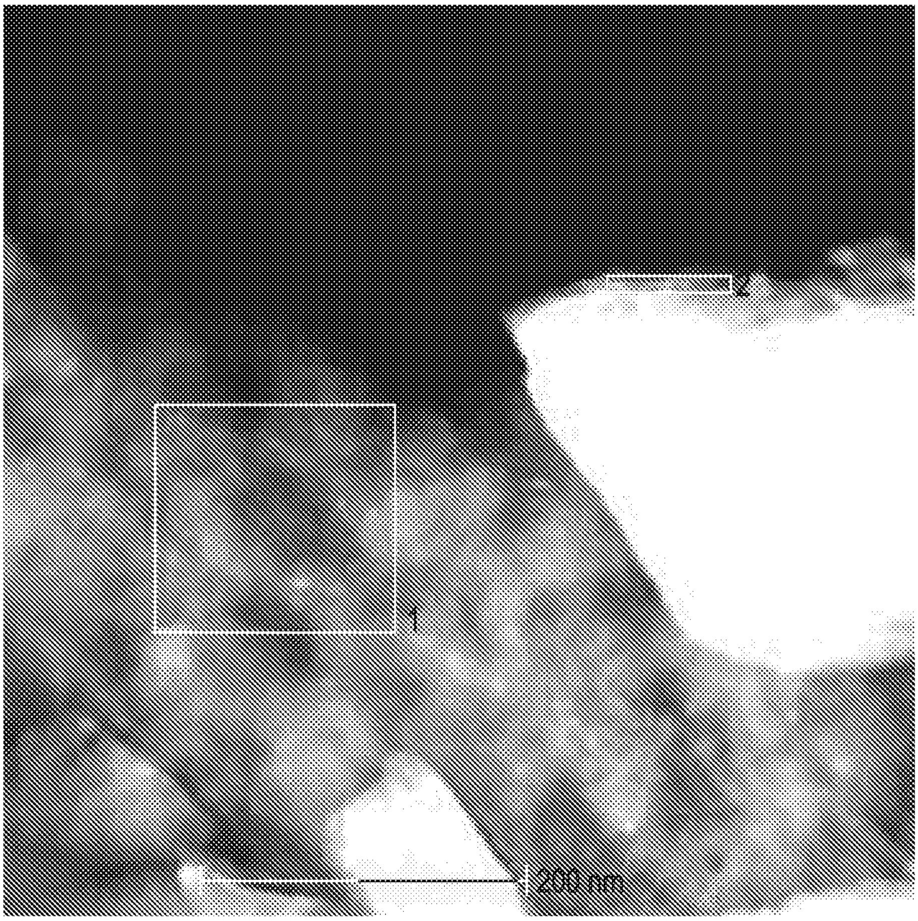


FIG. 9

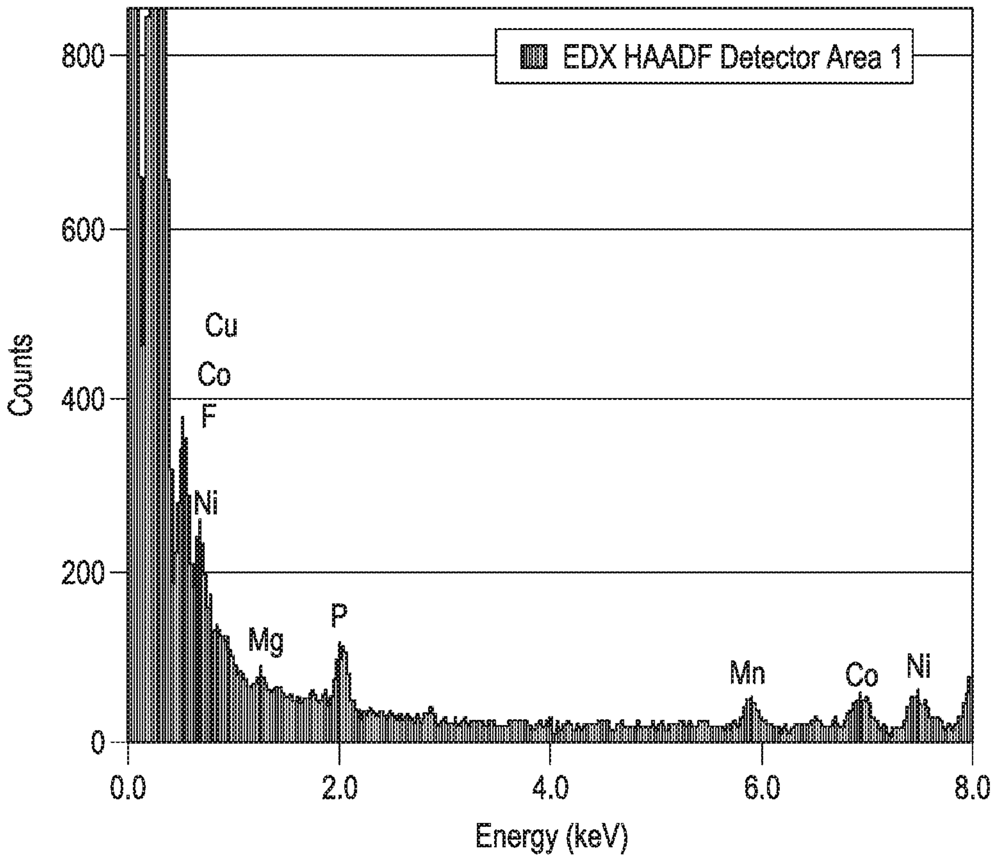

EDX HAADF Detector Area 1
Counts
800
600
400
200
0
Cu
Co
F
Ni
Mg
P
Mn
Co
Ni
0.0
2.0
4.0
6.0
8.0
Energy (keV)

FIG. 10

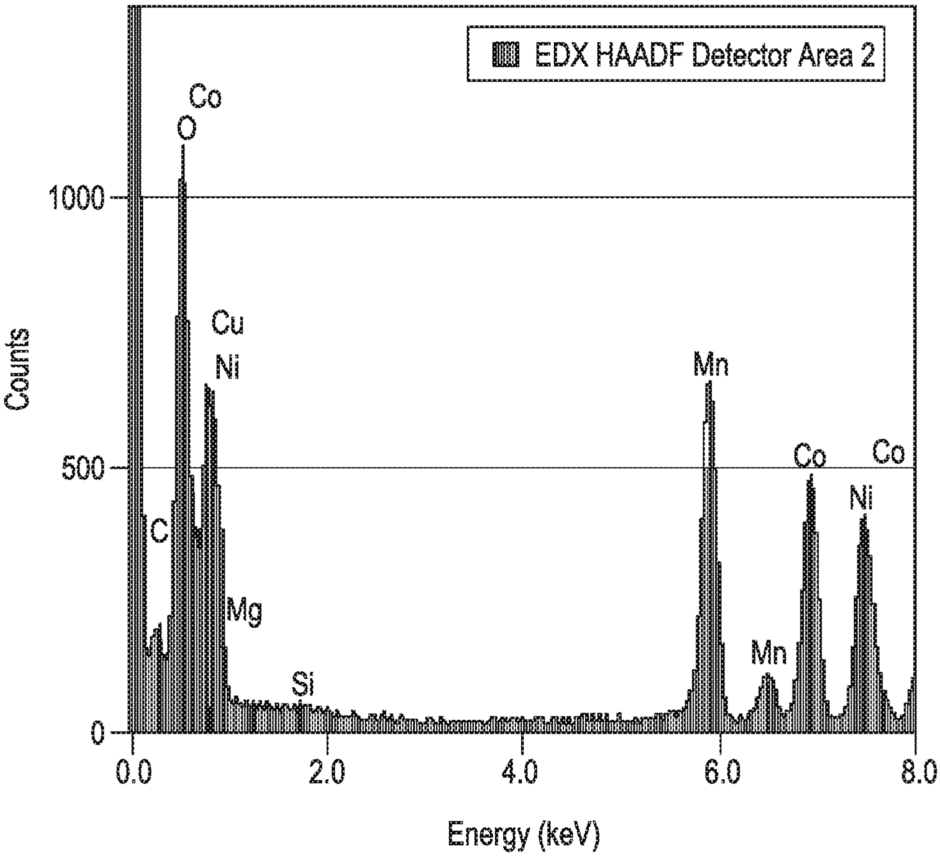

EDX HAADF Detector Area 2
Counts
1000
500
0
Co
O
Cu
Ni
C
Mg
Si
Mn
Mn
Co
Ni
Co
0.0
2.0
4.0
6.0
8.0
Energy (keV)

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/065585

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/485 H01M4/505 H01M4/525 H01M4/587 H01M10/0525
H01M10/0567 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)
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, BIOSIS, EMBASE, 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	EP 0 641 739 A1 (NISSAN CHEMICAL IND LTD [JP]) 8 March 1995 (1995-03-08) column 10, line 1-column 11, line 58 -----	1,10-13, 25
X	WO 2015/068324 A1 (SONY CORP [JP]) 14 May 2015 (2015-05-14)	1,13, 16-20, 23,24
Y	Paragraphs 167-171,220; page 23 examples examples 1-27, 1-28 and 1-29. Claims 16, 17 & EP 3 067 980 A1 (SONY CORP [JP]) 14 September 2016 (2016-09-14) paragraphs 168-172, 176, 221; page 23 examples examples 1-27, 1-28 and 1-29. Claims 16, 17. ----- -/--	2-9,14, 15,21,22

☒ 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 30 January 2017	Date of mailing of the international search report 07/02/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bettio, Andrea

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/065585

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/033595 A1 (DU PONT [US]; CHEN XUDONG [US]; LIU JUN J [US]; ROELOFS MARK GERRIT [U) 7 March 2013 (2013-03-07) Claims 1, 11; page 33-page 34, line 10 -----	2-9,15, 21,22
Y	US 2008/026297 A1 (CHEN ZONGHAI [US] ET AL) 31 January 2008 (2008-01-31) Claims 1, 2; paragraphs 51, 54, 55, 70 -----	14

2

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0641739 A1	08-03-1995	DE 69419091 D1	22-07-1999
		DE 69419091 T2	14-10-1999
		EP 0641739 A1	08-03-1995
		JP H0769620 A	14-03-1995
		US 5552083 A	03-09-1996
		US 5667725 A	16-09-1997
		US 5891565 A	06-04-1999
WO 2015068324 A1	14-05-2015	CN 105684205 A	15-06-2016
		EP 3067980 A1	14-09-2016
		JP 2015090777 A	11-05-2015
		KR 20160081904 A	08-07-2016
		US 2016248115 A1	25-08-2016
		WO 2015068324 A1	14-05-2015
WO 2013033595 A1	07-03-2013	CA 2844796 A1	07-03-2013
		CN 103765659 A	30-04-2014
		EP 2751865 A1	09-07-2014
		JP 2014525667 A	29-09-2014
		KR 20140060324 A	19-05-2014
		US 2014248529 A1	04-09-2014
		WO 2013033595 A1	07-03-2013
US 2008026297 A1	31-01-2008	AT 517448 T	15-08-2011
		CA 2638690 A1	23-02-2009
		CN 101373849 A	25-02-2009
		EP 2031690 A1	04-03-2009
		JP 5096263 B2	12-12-2012
		JP 2009054587 A	12-03-2009
		KR 20090020517 A	26-02-2009
		TW 200919805 A	01-05-2009
		US 2008026297 A1	31-01-2008