



## (51) International Patent Classification:

H01M 10/052 (2010.01) H01M 6/16 (2006.01)  
H01M 10/0568 (2010.01) H01M 10/054 (2010.01)  
H01M 10/0569 (2010.01)

## (21) International Application Number:

PCT/EP2015/067564

## (22) International Filing Date:

30 July 2015 (30.07.2015)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

14306218.0 31 July 2014 (31.07.2014) EP

(71) Applicants: WESTFÄLISCHE WILHELMS-UNIVERSITÄT MÜNSTER [DE/DE]; Schlossplatz 2, 48149 Münster (DE). INSTITUT POLYTECHNIQUE DE GRENOBLE [FR/FR]; 46 avenue Félix Viallet, F-38031 Grenoble (FR).

(72) Inventors: BRESSER, Dominic; Faulhaberstraße 14, 89073 Ulm (DE). KALHOFF, Julian; Von-Esmarch-Str. 171, 48149 Münster (DE). PASSERINI, Stefano; Am Schlossgarten 40, 48149 Münster (DE). SANCHEZ, Jean-

Yves; Le Chaboud, 781 Chemin de Chartreuse, F-38330 Saint-Ismier (FR). ALLOIN, Fannie; Chemin de la Mil-laudière, F-38220 Vizille (FR). BOLLOLI, Marco; 45, avenue Jeanne d'Arc, F-38100 Grenoble (FR).

(74) Agent: MICHALSKI HÜTTERMANN & PARTNER PATENTANWÄLTE MBB; Speditionstraße 21, Düsseldorf 40221 (DE).

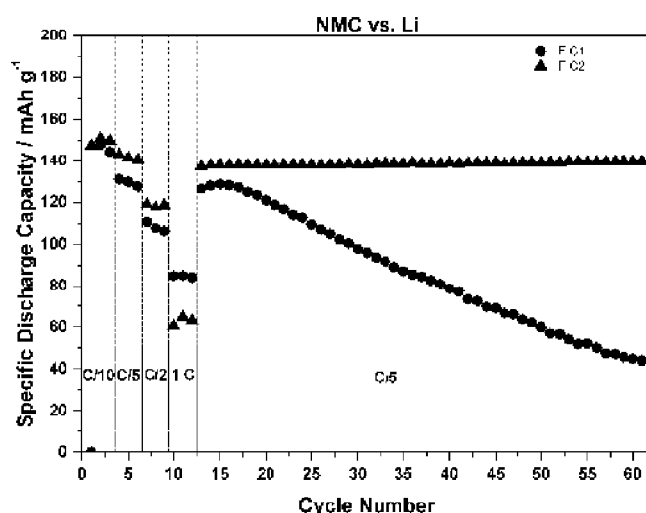
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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,

[Continued on next page]

## (54) Title: FLUORINATED CARBAMATES AS SOLVENT FOR LITHIUM-ION ELECTROLYTES

Figure 5



(57) Abstract: The present invention relates to an electrolyte solution comprising an electrolyte salt and an electrolyte solvent, wherein the electrolyte solvent comprises a fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$  in an amount in the range from  $\geq 80$  wt% to  $\leq 100$  wt %, referring to a total amount of the electrolyte solvent of 100 wt%, and to a method for preventing aluminum current collector corrosion in alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage devices by using an electrolyte solution comprising a fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$ .



LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, **Published:**

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, — *with international search report (Art. 21(3))*  
GW, KM, ML, MR, NE, SN, TD, TG).

---

### Fluorinated Carbamates as Solvent for Lithium-ion Electrolytes

---

The present invention relates to an electrolyte solution for use in lithium-ion batteries and particularly to an electrolyte solvent for use with sulfonimides and other electrolyte salts suffering aluminum current collector corrosion.

5     Lithium-ion batteries are nowadays the leading battery technology, since they offer efficient and high energy storage as well as high power density, and thus dominate the market for batteries used in portable electronic devices. However, one of the major safety issues of lithium-ion battery technology is related to the use of  $\text{LiPF}_6$  as lithium salt in currently commercially available batteries.  $\text{LiPF}_6$  is thermally unstable, resulting in the formation of gaseous  $\text{PF}_5$  that is a strong Lewis acid.  $\text{LiPF}_6$  hydrolysis moreover results in the formation of HF, which is not only highly toxic, but furthermore  
10     has a deleterious effect on the electrolyte solvent as well as the electrodes active materials. A major advantage of  $\text{LiPF}_6$  relative to other lithium salts, besides a well-balanced combination of chemical and electrochemical properties, however, is an initial surface passivation of the aluminum current collector, which is commonly used for lithium-ion cathodes as well as high voltage lithium-ion anodes  
15     as, for instance,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) provides a promising alternative as conducting salt since it provides a high ionic conductivity and a significantly improved thermal, chemical and electrochemical stability relatively to  $\text{LiPF}_6$ . However, LiTFSI severely suffers anodic dissolution, i.e.,  
20     “corrosion”, of the aluminum current collector. This corrosion results in a rapid fading of the lithium cell upon cycling, thus, preventing the use of the electrochemically, chemically, and thermally more stable LiTFSI rather than the toxic, unstable, and hazardous  $\text{LiPF}_6$  as conducting salt.

- 2 -

Document US 6159640 discloses electrolyte systems for lithium batteries of increased safety comprising partially fluorinated carbamates of the formula  $R^1R^2NC(O)OCR^3$  that show beneficial effects as solvent basically related to an increasing boiling and flash point. These effects relate to the whole class of the partially fluorinated carbamates.

The object underlying the present invention was to provide compounds usable for the suppression or prevention of the aluminum current collector corrosion resulting from the use of lithium salts such as LiTFSI and other electrolyte salts suffering aluminum current collector corrosion in electrolytes.

The problem is solved by an electrolyte solution comprising an electrolyte salt and an electrolyte solvent, wherein the electrolyte solvent comprises at least one fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the provision that when one of  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is H or a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

$R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $C_1$ - $C_3$ -alkyl and the ring carbon atoms being optionally substituted with  $C_1$ - $C_3$ -alkyl, wherein said heterocycle or  $C_1$ - $C_3$ -alkyl groups are optionally substituted by at least one fluorine atom;

$R^3$  is selected from the group comprising H, F, CN, perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl, and

wherein the electrolyte solvent comprises the fluorinated carbamate in an amount in the range from  $\geq 80$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%, and

wherein the electrolyte salt is selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal,

- 3 -

Al or Zn salts of  $-\text{CF}_3$  and  $-\text{CN}$ -substituted Hückel-anions, secondary carbanions substituted by  $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$ , tertiary carbanions substituted by  $(\text{CF}_3\text{SO}_2)_3\text{C}^-$ ,  $(\text{N}\equiv\text{C})_3\text{C}^-$  or  $(\text{FSO}_2)_3\text{C}^-$ , pentacyano cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $\text{SO}_3^-$ -end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts.

5

Surprisingly, it was found that the fluorinated carbamates  $\text{R}^1\text{R}^2\text{NC(O)OCR}^3\text{R}^4\text{R}^5$  according to the general formula (1) markedly suppress or prevent aluminum current collector corrosion.

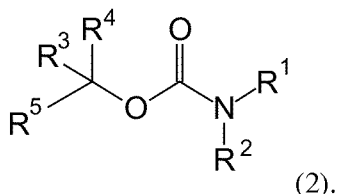
Advantageously, even after 100 potentiodynamic cyclic sweeps using LiTFSI as the electrolyte salt and 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate or 1,1,1,3,3,3-hexafluoropropan-2-yl

10 diethylcarbamate as the electrolyte solvent no aluminum corrosion was observed on the aluminum foil current collector. The prevention of aluminum current collector corrosion improves the safety of lithium-ion batteries, particularly with respect to large scale applications such as electric vehicles or stationary energy storage.

15 The beneficial effect of passivating the aluminum current collector and, thus, a stable cycling performance was, however, surprisingly only observed for fluorinated carbamates wherein the substituents  $\text{R}^4$  and  $\text{R}^5$  both are perfluorinated alkyl groups. Lesser fluorinated carbamates such as N,N-dimethyl trifluoroethyl carbamate wherein only one of  $\text{R}^4$  and  $\text{R}^5$  is a trifluoromethyl group and the other is hydrogen, did not show this beneficial effect, resulting in a rapidly fading electrochemical

20 performance.

The corresponding chemical formula of the fluorinated carbamate  $\text{R}^1\text{R}^2\text{NC(O)OCR}^3\text{R}^4\text{R}^5$  is given below:



25

The term "perfluorinated" alkyl group as used herein refers to alkyl groups wherein all carbon-bound hydrogen atoms are substituted by fluorine.

- 4 -

The term "alkyl" according to the invention is to be understood as including straight-chain or linear and branched alkyl groups, if not defined otherwise. The term "C<sub>1</sub>-C<sub>4</sub>-alkyl" as used herein refers to straight-chain or branched alkyl groups having 1 to 4 carbon atoms.

5

The term "branched C<sub>3</sub>-C<sub>4</sub>-alkyl" as used herein refers to branched alkyl groups having 3 to 4 carbon atoms. A branched C<sub>3</sub>-C<sub>4</sub>-alkyl group may be selected from the group comprising isopropyl, isobutyl (2-methylpropyl), sec-butyl (1-methylpropyl) and/or tert-butyl (1,1-dimethylethyl). Linear or straight-chain C<sub>1</sub>-C<sub>4</sub>-alkyl groups may be selected from the group comprising methyl, ethyl, n-propyl and/or n-butyl.

10

The term "C<sub>3</sub>-C<sub>7</sub>-cycloalkyl" as used herein refers to the group comprising cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and/or cycloheptyl.

15 Embodiments wherein the substituents R<sup>1</sup> and R<sup>2</sup> are directly linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle may refer to substituents selected from the group comprising aziridinyl, azetidiny, pyrrolidinyl, piperidinyl and/or azepanyl. Embodiments wherein the substituents R<sup>1</sup> and R<sup>2</sup> are linked via one or more additional nitrogen and/or oxygen atoms to form together with the nitrogen atom to which they are attached a 3-  
20 to 7-membered non aromatic heterocycle may refer to substituents selected from the group comprising oxaziridinyl, diaziridinyl, 1,3-oxazetidiny, 1,3-diazetidiny, oxazolidinyl, diazolidinyl, morpholinyl (tetrahydro-1,4-oxazinyl) and/or tetrahydro-1,4-diazinyl.

20

The substituents R<sup>1</sup> and R<sup>2</sup> in embodiments may be selected, the same or independently of the other,  
25 from the group comprising linear C<sub>1</sub>-C<sub>4</sub>-alkyl, branched C<sub>3</sub>-C<sub>4</sub>-alkyl and/or C<sub>3</sub>-C<sub>7</sub>-cycloalkyl, with the provision that when one of R<sup>1</sup> or R<sup>2</sup> is C<sub>3</sub>-C<sub>7</sub>-cycloalkyl the other is a C<sub>1</sub>-C<sub>2</sub> alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom. The substituents R<sup>1</sup> and R<sup>2</sup> may be linked together to form a 3- to 7-membered non aromatic heterocyclic ring, or may be selected from linear C<sub>1</sub>-C<sub>4</sub>-alkyl, branched C<sub>3</sub>-C<sub>4</sub>-alkyl or cycloalkyl rings. The provision that when  
30 one of R<sup>1</sup> or R<sup>2</sup> is C<sub>3</sub>-C<sub>7</sub>-cycloalkyl the other is hydrogen or a C<sub>1</sub>-C<sub>2</sub> alkyl group provides a sufficient

30

- 5 -

viscosity of the compound. The alkyl or cycloalkyl groups of  $R^1$  and  $R^2$  are optionally substituted by one or more fluorine atoms. It has been found that for effectively preventing aluminum current collector corrosion, however, at least the substituents  $R^4$  and  $R^5$  should be a perfluorinated linear  $C_1$ - $C_4$ - or branched  $C_3$ - $C_4$ -alkyl group.

5

The substituent  $R^3$  may be selected from the group comprising H, F, CN, and perfluorinated methyl, ethyl, n-propyl, n-butyl, isopropyl, isobutyl, sec-butyl and/or tert-butyl. The substituent  $R^3$  may particularly be selected from H, F, and perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $R^3$  is selected from the group comprising H, F and/or perfluorinated linear  $C_1$ - $C_3$ -alkyl.

10 Preferably  $R^3$  is selected from the group comprising H, F,  $CF_3$  and/or  $C_2F_5$ .  $R^3$  particularly may be hydrogen. Anodic aluminium dissolution was prevented using carbamates wherein  $R^3$  was hydrogen. The substituent  $R^3$  being hydrogen further provides the benefit of cost efficiency as fluorination generally increases the production costs.

15 The substituents  $R^4$  and  $R^5$  may be identical or different from each other selected from the group comprising perfluorinated methyl, ethyl, n-propyl or n-butyl, or isopropyl, isobutyl, sec-butyl and/or tert-butyl. The substituents  $R^4$  and  $R^5$  particularly may be identical or different from each other selected from perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $R^4$  and  $R^5$  are the same or independently of the other perfluorinated linear  $C_1$ - $C_3$ -alkyl, preferably selected from  
20 the group comprising  $CF_3$  and/or  $C_2F_5$ . Good results in the prevention of anodic aluminum dissolution and prevention of corrosion of aluminum current collectors were observed in LiTFSI-containing electrolytes using carbamates with  $R^4$  and  $R^5$  being  $CF_3$  or  $C_2F_5$ .

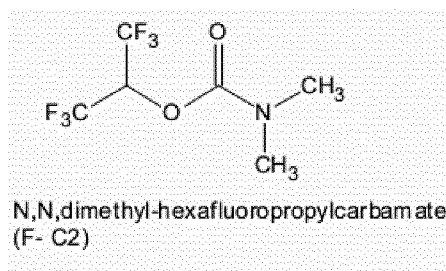
The substituents  $R^1$  and  $R^2$  may be identical or different from each other selected from linear  $C_1$ - $C_4$ -  
25 alkyl or branched  $C_3$ - $C_4$ -alkyl. One or more hydrogen atom of the alkyl groups may be substituted by a fluorine atom. The alkyl groups alternatively may not be substituted by fluorine atoms, and thus reduce production costs. In preferred embodiments,  $R^1$  and  $R^2$  are selected, the same or independently of the other, from the group comprising linear or branched  $C_1$ - $C_3$ -alkyl, preferably selected from the group comprising methyl and/or ethyl. Small and particularly not fluorinated substituents  $R^1$  and  $R^2$

- 6 -

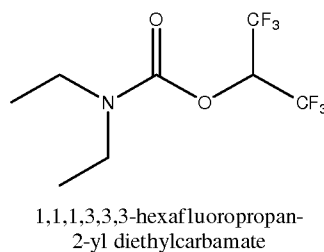
provide advantages in view of cost efficient carbamates, solubility of the electrolyte salt, and low viscosity of the electrolyte solvent.

In an embodiment, the fluorinated carbamate is selected from the group comprising 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate, 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate and mixtures thereof. 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate is also denoted N,N-dimethyl-hexafluoropropylcarbamate (F-C2). 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate is also denoted N,N-diethyl-hexafluoropropylcarbamate (F-C4).

The corresponding chemical formulas of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate or N,N-dimethyl-hexafluoropropylcarbamate (F-C2) and 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4), respectively, are given below:



(3)



(4).

It could be shown that particularly a use of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) and 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte solvent for electrolytes containing LiTFSI as the electrolyte salt resulted in the prevention of anodic aluminum dissolution and no corrosion was observed for the aluminum foil used as current collector, even after 100 potentiodynamic cyclic sweeps.

The electrolyte solution comprises at least one fluorinated carbamate according to the general formula (1). In embodiments, the electrolyte solution may comprise a mixture of fluorinated carbamates.

The fluorinated carbamate according to the general formula (1) is usable for the prevention of aluminum current collector corrosion in an alkali metal or alkaline earth metal-based electrochemical

- 7 -

energy storage device containing sulfonimides or other electrolyte salts suffering aluminum current collector corrosion. The fluorinated carbamate may be the sole electrolyte solvent used in an electrolyte solution. A determination of the amount of fluorinated carbamate necessary for a clear improvement in the passivation of an aluminum current collector showed that an amount of  $\geq 80$  wt.-% of fluorinated carbamate such as 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) or 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) in standard non-fluorinated carbonates significantly reduced the aluminum current collector corrosion. Referring to non-fluorinated carbonate solvents, aluminum passivation within the first 10 cycles by using 80 wt% of F-C2 or F-C4 could be achieved, while amounts of 33 wt% or 50 wt%, referring to the total weight of the electrolyte solvent, in standard non-fluorinated carbonates did not sufficiently suppress aluminum current collector corrosion. In embodiments, the electrolyte solution comprises the fluorinated carbamate in a range from  $\geq 85$  wt% to  $\leq 100$  wt%, preferably in a range of  $\geq 90$  wt% to  $\leq 100$  wt%, more preferably in a range of  $\geq 95$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%. If not indicated otherwise, the ratios of electrolyte solvents or compounds as given refer to a respective weight ratio. Weight percent, abbreviated wt% or wt.-% are synonyms that refer to the concentration of a compound as the weight of the compound divided by the weight of the composition and multiplied by 100. The total amount of all solvents of the electrolyte solution does not exceed 100 wt%.

The fluorinated carbamates are usable for the inhibition of aluminum current collector corrosion together with electrolyte solvents such as carbonates, esters, lactones or nitriles, in particular with non-fluorinated organic carbonates. This is of particular benefit as non-fluorinated organic carbonates are used as standard solvents in commercial lithium-ion batteries. In embodiments, the electrolyte solution comprises at least one non-fluorinated organic carbonate selected from the group comprising ethylene carbonate, ethyl methyl carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and mixtures thereof. A preferred mixture of carbonate solvents is a carbonate solvent mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC), for example in a weight ratio of 1:1.

The electrolyte solvent is advantageously usable with sulfonimides and other electrolyte salts suffering aluminum current collector corrosion. Such salts preferably are selected from the group comprising

- 8 -

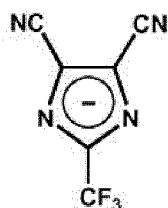
alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate and oxalatoborate salts. Further preferred salts may be selected from the group comprising alkali or alkaline earth metal, Al or Zn salts of  $\text{CF}_3^-$  and CN-substituted Hückel-anions, of secondary carbanions substituted with  $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$ , of tertiary carbanions substituted with  $(\text{CF}_3\text{SO}_2)_3\text{C}^-$ ,  $(\text{N}\equiv\text{C})_3\text{C}^-$  or  $(\text{FSO}_2)_3\text{C}^-$ ,  
 5 pentacyano cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $\text{SO}_3^-$ -end-capped polyethylene glycol, or sulfonamide end-capped polyethylene glycol, and mixtures of these salts. The alkali or alkaline earth metal salt preferably is selected from lithium, sodium, potassium, magnesium, or calcium salts. The electrolyte salt particularly is a lithium salt.

- 10 In a preferred embodiment, the alkali or alkaline earth metal sulfonimide or sulfonate salt is a lithium salt selected from the group comprising lithium bis(trifluoromethanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI), lithium bis(fluorosulfonyl)imide  $\text{LiN}(\text{FSO}_2)_2$  (LiFSI), lithium (trifluoromethylsulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (fluorosulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{F})(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (nonafluoro butan-2-one sulfonyl)(trifluoromethylsulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{CF}_3)$ , lithium (nonafluoro butan-2-one sulfonyl)(fluorosulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{F})$  and/or lithium trifluoromethanesulfonate  $\text{Li}(\text{CF}_3)\text{SO}_3$  (LiTf). Preferred lithium sulfonimide salts are bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(fluorosulfonyl)imide (LiFSI). A preferred methide salt is  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ . A preferred oxalatoborate salt is lithium bis(oxalato)borate  
 15 20 (LiBOB).

Particularly sulfonimide salts provide a high ionic conductivity and show enhanced thermal and electrochemical stability and prevent an immediate formation of HF by hydrolysis as may occur with  $\text{LiPF}_6$ . Particularly, the anodic aluminum dissolution, to which usually is referred to herein as  
 25 “corrosion”, can be prevented by using a fluorinated carbamate according to the invention. A use of sulfonimide salts such as LiTFSI will result in significantly safer lithium-ion batteries. Particularly LiTFSI, LiFSI and the sulfonate Li-Triflate, which are known to suffer anodic aluminum dissolution, can advantageously be utilized as electrolyte salts in lithium-ion batteries using a fluorinated carbamate according to the invention as the solvent.

- 9 -

A preferred  $-\text{CF}_3$  and  $-\text{CN}$ -substituted Hückel-anion is 4,5-dicyano-2-(trifluoromethyl)imidazolid, the anion according to the following formula (5)



- 5 Other anions of electrolyte salts are secondary carbanions substituted by electron-withdrawing groups such as  $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$  and tertiary carbanions substituted by electron-withdrawing groups such as  $(\text{CF}_3\text{SO}_2)_3\text{C}^-$  which is also denoted methide,  $(\text{N}\equiv\text{C})_3\text{C}^-$  or  $(\text{FSO}_2)_3\text{C}^-$ , and aromatic anions such as pentacyano cyclopentadienyl  $(\text{N}\equiv\text{C})_5\text{C}_5^-$ .
- 10 The term "arylsulfonyl, trifluoromethane sulfonyl amide anion" according to the invention is to be understood as meaning an anion  $(\text{X}-\text{C}_6\text{H}_4-\text{SO}_2)(\text{C}_n\text{F}_{2n+1}\text{SO}_2)\text{N}^-$  wherein X is selected from the group of electron-donating substituents methyl, methoxy and/or amine or the group of electron-withdrawing groups nitrile, nitro and/or  $\text{CF}_3\text{SO}_2$ , or X is a functionality allowing its polymerization such as a double bond (vinyl) or an epoxy group.
- 15 The term " $\text{SO}_3^-$ -end-capped polyethylene glycol" according to the invention is to be understood as meaning monomethyl PEG end-capped by one or two ionic moieties according to the formula (6)  $\text{CH}_3-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{O}-\text{SO}_3^-$  wherein  $1 \leq n \leq 23$  and preferably  $3 \leq n \leq 8$  and, alternatively, PEG twice end-capped by  $\text{SO}_3^-$  according to the formula (7)  $^- \text{O}_3\text{S}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{O}-\text{SO}_3^-$  wherein  $1 \leq n \leq 46$  and
- 20 preferably  $8 \leq n \leq 20$ .

The electrolyte solvent may be a liquid or an ionic liquid, for example based on the anions above. The electrolyte can fill a porous separator or it can be a gelled electrolyte as a copolymer poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) or a polymethacrylonitrile network.

- 25 Another aspect of the invention refers to an alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device, particularly a lithium battery, a primary or

- 10 -

secondary lithium-ion battery, a lithium polymer battery or a lithium-ion capacitor, comprising an electrolyte solution according to the invention. The term "energy storage device" comprises primary and secondary, i.e., rechargeable batteries. However, rechargeable batteries or accumulators are also denoted with the term "battery" which usually is used as a generic term. Hence, for simplicity if not  
 5 denoted otherwise, in the present invention the term "battery" is used synonymous to also designate "accumulators". Preferably, the electrolyte solution according to the invention is usable for a primary or secondary lithium-ion battery or a lithium polymer battery. A lithium-ion battery for example comprises a first electrode of a cathodic material, a second electrode of an anodic material and an electrolyte. Advantageously, an electrochemical energy storage device, particularly a secondary  
 10 lithium battery, comprising the electrolyte solution according to the invention provides increased safety.

The electrolyte solution comprises an electrolyte salt and an electrolyte solvent, wherein the electrolyte solvent comprises at least one fluorinated carbamate according to the general formula (1)

15  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the provision that when one of  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is H or a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

20  $R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $C_1$ - $C_3$ -alkyl and the ring carbon atoms being optionally substituted with  $C_1$ - $C_3$ -alkyl, wherein said heterocycle or  $C_1$ - $C_3$ -alkyl groups are optionally substituted by at least one fluorine atom;

25  $R^3$  is selected from the group comprising H, F, CN, perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl, and

wherein the electrolyte solvent comprises the fluorinated carbamate in an amount in the range from  $\geq$   
 30 80 wt% to  $\leq$  100 wt%, referring to a total amount of the electrolyte solvent of 100 wt%, and

- 11 -

wherein the electrolyte salt is selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of  $-\text{CF}_3$  and  $-\text{CN}$ -substituted Hückel-anions, secondary carbanions substituted by  $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$ , tertiary carbanions substituted by  $(\text{CF}_3\text{SO}_2)_3\text{C}^-$ ,  $(\text{N}\equiv\text{C})_3\text{C}^-$  or  $(\text{FSO}_2)_3\text{C}^-$ , pentacyano  
5 cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $\text{SO}_3^-$ -end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts.

The substituent  $\text{R}^3$  may be selected from the group comprising H, F, CN, and perfluorinated methyl, ethyl, n-propyl, n-butyl, isopropyl, isobutyl, sec-butyl and/or tert-butyl. The substituent  $\text{R}^3$  may  
10 particularly be selected from H, F, and perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $\text{R}^3$  is selected from the group comprising H and/or perfluorinated linear  $\text{C}_1$ - $\text{C}_3$ -alkyl. Preferably  $\text{R}^3$  is selected from the group comprising H,  $\text{CF}_3$  and/or  $\text{C}_2\text{F}_5$ .  $\text{R}^3$  particularly may be hydrogen. The substituents  $\text{R}^4$  and  $\text{R}^5$  may be identical or different from each other selected from the group comprising perfluorinated methyl, ethyl, n-propyl or n-butyl, or isopropyl, isobutyl, sec-butyl  
15 and/or tert-butyl. The substituents  $\text{R}^4$  and  $\text{R}^5$  particularly may be identical or different from each other selected from perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $\text{R}^4$  and  $\text{R}^5$  are the same or independently of the other perfluorinated linear  $\text{C}_1$ - $\text{C}_3$ -alkyl, preferably selected from the group comprising  $\text{CF}_3$  and/or  $\text{C}_2\text{F}_5$ .

20 The substituents  $\text{R}^1$  and  $\text{R}^2$  in embodiments may be selected, the same or independently of the other, from the group comprising linear  $\text{C}_1$ - $\text{C}_4$ -alkyl, branched  $\text{C}_3$ - $\text{C}_4$ -alkyl and/or  $\text{C}_3$ - $\text{C}_7$ -cycloalkyl, with the provision that when one of  $\text{R}^1$  or  $\text{R}^2$  is  $\text{C}_3$ - $\text{C}_7$ -cycloalkyl the other is a  $\text{C}_1$ - $\text{C}_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom. The substituents  $\text{R}^1$  and  $\text{R}^2$  may be identical or different from each other selected from linear  $\text{C}_1$ - $\text{C}_4$ -alkyl or branched  $\text{C}_3$ -  
25  $\text{C}_4$ -alkyl. One or more hydrogen atom of the alkyl groups may be substituted by a fluorine atom. The alkyl groups alternatively may not be substituted by fluorine atoms, and thus reduce production costs. In preferred embodiments,  $\text{R}^1$  and  $\text{R}^2$  are selected, the same or independently of the other, from the group comprising linear or branched  $\text{C}_1$ - $\text{C}_3$ -alkyl, preferably selected from the group comprising methyl and/or ethyl.

- 12 -

In an embodiment, the fluorinated carbamate is selected from the group comprising 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate, 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate and mixtures thereof.

5 In embodiments, the electrolyte solution comprises the fluorinated carbamate in a range from  $\geq 85$  wt% to  $\leq 100$  wt%, preferably in a range of  $\geq 90$  wt% to  $\leq 100$  wt%, more preferably in a range of  $\geq 95$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%. The fluorinated carbamates are usable for the inhibition of aluminum current collector corrosion together with electrolyte solvents such as carbonates, esters, lactones or nitriles, in particular with non-  
10 fluorinated organic carbonates. In embodiments, the electrolyte solution comprises at least one non-fluorinated organic carbonate selected from the group comprising ethylene carbonate, ethyl methyl carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and mixtures thereof. A preferred mixture of carbonate solvents is a carbonate solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), for example in a weight ratio of 1:1.

15 The electrolyte solvent is advantageously usable with sulfonimides and other electrolyte salts suffering aluminum current collector corrosion. Such salts preferably are selected from the group comprising alkali or alkaline earth metal sulfonimide, methide, sulfonate and oxalatoborate salts. In a preferred embodiment, the alkali or alkaline earth metal sulfonimide or sulfonate salt is a lithium salt selected  
20 from the group comprising lithium bis(trifluoromethanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI), lithium bis(fluorosulfonyl)imide  $\text{LiN}(\text{FSO}_2)_2$  (LiFSI), lithium (trifluoromethylsulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (fluorosulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{F})(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (nonafluoro butan-2-one sulfonyl)(trifluoromethylsulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{CF}_3)$ , lithium (nonafluoro butan-  
25 2-one sulfonyl)(fluorosulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{F})$  and/or lithium trifluoromethanesulfonate  $\text{Li}(\text{CF}_3)\text{SO}_3$  (LiTf). Preferred lithium sulfonimide salts are bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(fluorosulfonyl)imide (LiFSI). A preferred methide salt is  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ . A preferred oxalatoborate salt is lithium bis(oxalato)borate (LiBOB).

30

Another aspect of the invention refers to a method for preventing aluminum current collector corrosion in an alkali or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device containing an electrolyte solution comprising an electrolyte salt and an electrolyte solvent, the method comprising the step of using an electrolyte solvent comprising in a range from  $\geq 80$  wt% to  $\leq$  100 wt%, referring to a total amount of the electrolyte solvent of 100 wt%, of at least one fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the provision that when one of  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is H or a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

$R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $C_1$ - $C_3$ -alkyl and the ring carbon atoms being optionally substituted with  $C_1$ - $C_3$ -alkyl, wherein said heterocycle or  $C_1$ - $C_3$ -alkyl groups are optionally substituted by at least one fluorine atom;

$R^3$  is selected from the group comprising H, F, CN, perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl, and

wherein the electrolyte salt is selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of  $-CF_3$  and  $-CN$ -substituted Hückel-anions, secondary carbanions substituted by  $(CF_3SO_2)_2CH^-$ , tertiary carbanions substituted by  $(CF_3SO_2)_3C^-$ ,  $(N\equiv C)_3C^-$  or  $(FSO_2)_3C^-$ , pentacyano cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $SO_3^-$ -end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts.

Advantageously, the method increases the safety of an electrochemical energy storage device, particularly a lithium battery, a primary or secondary lithium-ion battery, a lithium polymer battery or a lithium-ion capacitor. Preferably, the device is a primary or secondary lithium-ion battery or a lithium polymer battery.

Another aspect of the invention refers to the use of a fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear C<sub>1</sub>-C<sub>4</sub>-alkyl, branched C<sub>3</sub>-C<sub>4</sub>-alkyl and/or C<sub>3</sub>-C<sub>7</sub>-cycloalkyl, with the provision that when one of  $R^1$  or  $R^2$  is C<sub>3</sub>-C<sub>7</sub>-cycloalkyl the other is H or a C<sub>1</sub>-C<sub>2</sub> alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

$R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with C<sub>1</sub>-C<sub>3</sub>-alkyl and the ring carbon atoms being optionally substituted with C<sub>1</sub>-C<sub>3</sub>-alkyl, wherein said heterocycle or C<sub>1</sub>-C<sub>3</sub>-alkyl groups are optionally substituted by at least one fluorine atom;

$R^3$  is selected from the group comprising H, F, CN, perfluorinated linear C<sub>1</sub>-C<sub>4</sub>-alkyl and/or perfluorinated branched C<sub>3</sub>-C<sub>4</sub>-alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated linear C<sub>1</sub>-C<sub>4</sub>-alkyl and/or perfluorinated branched C<sub>3</sub>-C<sub>4</sub>-alkyl,

for the prevention of aluminum current collector corrosion in an alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device, containing an electrolyte solution comprising an electrolyte salt selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of -CF<sub>3</sub> and -CN-substituted Hückel-anions, secondary carbanions substituted by (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>CH<sup>-</sup>, tertiary carbanions substituted by (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, (N≡C)<sub>3</sub>C<sup>-</sup> or (FSO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, pentacyano cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions, SO<sub>3</sub><sup>-</sup>-end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts, and an electrolyte solvent, wherein the fluorinated carbamate is used in an amount in the range from ≥ 80 wt% to ≤ 100 wt%, referring to a total amount of the electrolyte solvent of 100 wt%.

Referring to the method for preventing aluminum current collector corrosion in an alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device and/or to the use of a fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$ , the

- 15 -

substituent  $R^3$  may be selected from the group comprising H, F, CN, and perfluorinated methyl, ethyl, n-propyl, n-butyl, isopropyl, isobutyl, sec-butyl and/or tert-butyl. The substituent  $R^3$  may particularly be selected from H, F, and perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $R^3$  is selected from the group comprising H and/or perfluorinated linear  $C_1$ - $C_3$ -alkyl.

5 Preferably,  $R^3$  is selected from the group comprising H,  $CF_3$  and/or  $C_2F_5$ .  $R^3$  particularly may be hydrogen. The substituents  $R^4$  and  $R^5$  may be identical or different from each other selected from the group comprising perfluorinated methyl, ethyl, n-propyl or n-butyl, or isopropyl, isobutyl, sec-butyl and/or tert-butyl. The substituents  $R^4$  and  $R^5$  particularly may be identical or different from each other selected from perfluorinated methyl, ethyl, propyl or isopropyl. In preferred embodiments,  $R^4$  and  $R^5$   
10 are the same or independently of the other perfluorinated linear  $C_1$ - $C_3$ -alkyl, preferably selected from the group comprising  $CF_3$  and/or  $C_2F_5$ .

The substituents  $R^1$  and  $R^2$  in embodiments may be selected, the same or independently of the other, from the group comprising linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the  
15 provision that when one of  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom. The substituents  $R^1$  and  $R^2$  may be identical or different from each other selected from linear  $C_1$ - $C_4$ -alkyl or branched  $C_3$ - $C_4$ -alkyl. One or more hydrogen atom of the alkyl groups may be substituted by a fluorine atom. The alkyl groups alternatively may not be substituted by fluorine atoms, and thus reduce production costs.  
20 In preferred embodiments,  $R^1$  and  $R^2$  are selected, the same or independently of the other, from the group comprising linear or branched  $C_1$ - $C_3$ -alkyl, preferably selected from the group comprising methyl and/or ethyl.

In an embodiment, the fluorinated carbamate is selected from the group comprising 1,1,1,3,3,3-  
25 hexafluoropropan-2-yl dimethylcarbamate, 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate and mixtures thereof.

In embodiments, the electrolyte solution comprises the fluorinated carbamate in a range from  $\geq 85$   
wt% to  $\leq 100$  wt%, preferably in a range of  $\geq 90$  wt% to  $\leq 100$  wt%, more preferably in a range of  $\geq$   
30 95 wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%. The

- 16 -

fluorinated carbamates are usable for the inhibition of aluminum current collector corrosion together with electrolyte solvents such as carbonates, esters, lactones or nitriles, in particular with non-fluorinated organic carbonates. In embodiments, the electrolyte solution comprises at least one non-fluorinated organic carbonate selected from the group comprising ethylene carbonate, ethyl methyl  
 5 carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and mixtures thereof. A preferred mixture of carbonate solvents is a carbonate solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), for example in a weight ratio of 1:1.

The electrolyte solvent is advantageously usable with sulfonimides and other electrolyte salts suffering  
 10 aluminum current collector corrosion. Such salts preferably are selected from the group comprising alkali or alkaline earth metal sulfonimide, methide, sulfonate and oxalatoborate salts. In a preferred embodiment, the alkali or alkaline earth metal sulfonimide or sulfonate salt is a lithium salt selected from the group comprising lithium bis(trifluoromethanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI), lithium bis(fluorosulfonyl)imide  $\text{LiN}(\text{FSO}_2)_2$  (LiFSI), lithium  
 15 (trifluoromethylsulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (fluorosulfonyl)(nonafluorobutanesulfonyl)imide  $\text{LiN}(\text{SO}_2\text{F})(\text{SO}_2\text{C}_4\text{F}_9)$ , lithium (nonafluoro butan-2-one sulfonyl)(trifluoromethylsulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{CF}_3)$ , lithium (nonafluoro butan-2-one sulfonyl)(fluorosulfonyl)imide  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_5)(\text{SO}_2\text{F})$  and/or lithium trifluoromethanesulfonate  $\text{Li}(\text{CF}_3)\text{SO}_3$  (LiTf). Preferred lithium sulfonimide salts are  
 20 bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(fluorosulfonyl)imide (LiFSI). A preferred methide salt is  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ . A preferred oxalatoborate salt is lithium bis(oxalato)borate (LiBOB).

Unless otherwise defined, the technical and scientific terms used herein have the same meaning as  
 25 commonly understood by one of ordinary skill in the art to which this invention belongs.

The examples which follow serve to illustrate the invention in more detail but do not constitute a limitation thereof.

30 In the figures show:

- Figure 1 a cyclic voltammogram of a 1M solution of LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) for 100 cycles using aluminum as working electrode.
- Figure 2 potential profiles of an NMC half-cell for the cycles 15, 20, 25, 30 and 35 at C/5 a 1M solution of LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2), cut-off potentials: 3.0 and 4.3 V vs. Li/Li<sup>+</sup>.
- Figure 3 a cyclic voltammogram for a 1M solution of LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1) for 100 cycles using aluminum as working electrode.
- Figure 4 potential profiles of an NMC half-cell for the cycles 15, 20, 25, 30 and 35 at C/5 using a 1M solution of LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1) as electrolyte, cut-off potentials: 3.0 and 4.3 V vs. Li/Li<sup>+</sup>.
- Figure 5 a galvanostatic cycling comparison of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC)-based cathodes in half-cell configuration using 1M LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1, dots) or in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2, triangles) as electrolytes.
- Figure 6 a cyclic voltammogram for a 1M solution of LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) for 100 cycles using aluminum as working electrode.
- Figure 7 the galvanostatic cycling of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC)-based cathodes in half-cell configuration using 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte.
- Figure 8 potential profiles of a NMC half-cell for the cycles 15, 20, 25, 30 and 35 at C/5 using a 1M solution of LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte, cut-off potentials: 3.0 and 4.3 V vs. Li/Li<sup>+</sup>.
- Figure 9 cyclic voltammograms for 100 cycles using aluminum as working electrode in a 1M solution of LiTFSI in a solvent mixture of 33 wt% (1:1:1), 50 wt% (2:1:1) or 80 wt% (8:1:1) of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) in EC/DMC (1:1), in the figures 9a), 9b) and 9c), respectively.
- Figure 10 Electrochemical stability of a 1M solution of LiTFSI in N,N-dimethylethyl carbamate (C1), N,N-dimethyl trifluoroethyl carbamate (F-C1), 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2), or 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte towards oxidation using a Pt-wire as working electrode.

- 18 -

Figure 11 XPS analysis of potentiodynamically polarized aluminum foils in presence of different electrolyte compositions: (a) and (b) 1M LiTFSI in F-C2, (c) and (d) 1M LiTFSI in F-C4: panels (a) and (c) show the recorded Al 2p XPS spectra, panels (b) and (d) the corresponding evolution of the atomic concentration upon etching ( $\text{AlF}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_{\text{metal}}$ , and C).

#### Example 1

##### Synthesis of N,N-dimethyl trifluoroethyl carbamate (F-C1)

A suspension of 1.5 eq. sodium hydride (> 99%, Sigma-Aldrich) in freshly distilled tetrahydrofuran (> 99%, Sigma-Aldrich) was put in a round-bottom flask under inert atmosphere. The flask was then cooled down to 0 °C and kept under inert atmosphere for the entire length of the reaction. 1 eq. of 1,1,1-trifluoroethanol (>99% Acros Organics) was then added to the slurry under stirring, and after the formation of the alcoholate 1 eq. of N,N dimethyl carbamyl chloride (> 99%, Sigma-Aldrich) was added as well. The flask was gradually warmed to room temperature ( $25 \pm 2$  °C), and the reaction was carried on for 24 hours. At the end of the reaction, a solution of water saturated with  $\text{Na}_2\text{CO}_3$  was added, and several liquid extractions with diethyl ether were put in place. The organic phases were dried under magnesium sulfate and the carbamate was then obtained as a colorless liquid by distillation under reduced pressure at 100 mm Hg and room temperature.

#### Example 2

##### Synthesis of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2)

The preparation was carried out as described above in Example 1, but using 1 eq. of 1,1,1,3,3,3-hexafluoropropanol (>99% Acros Organics). 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate was obtained as a colorless liquid.

#### Example 3

##### Synthesis of 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4)

- 19 -

The preparation was carried out as described in example 1, but using 1 eq. of 1,1,1,3,3,3-hexafluoropropanol (>99% Acros Organics) and *N,N* diethyl carbamyl chloride (> 99% , Sigma-Aldrich). 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate was obtained as a colorless liquid.

## 5 Electrochemical characterization

Solvents and electrolyte solutions:

The electrolyte solvents *N,N*-dimethyl trifluoroethyl carbamate (F-C1), 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) and 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) were used as synthesized according to examples 1 to 3, respectively.

Ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC), all battery grade, were purchased at UBE Corporation and Ferro Corporation.

15 The conductive salt lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 3M) was set to 1 mol L<sup>-1</sup> for all investigated electrolyte compositions. Electrolyte solutions were prepared by mixing the solvents in their respective weight ratios and dissolving LiTFSI in an appropriate amount to yield a 1M solution.

Electrode preparation:

20 Positive electrodes were prepared by combining Li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> (NMC, Toda) as the active material, polyvinylidene fluoride (PVdF, Kynar<sup>®</sup> HSV 900, ARKEMA) as binder, and the conductive carbon additive Super C65<sup>®</sup> (TIMCAL). *N*-Methyl-2-pyrrolidone (NMP) was used as solvent for the PVdF binding agent. Electrode pastes were prepared using a Vario-Planetary Mill Pulverisette 4 (Fritsch). The resulting slurry was cast on aluminum foil (battery grade, 99.99% purity, Evonik),  
25 electrodes having a diameter of 12 mm were punched and subsequently dried at 120 °C for 24 h. The electrode final composition was 88 wt% NMC, 7 wt% conductive carbon, and 5 wt% PVdF. The average mass loading of the electrodes was about 7 mg cm<sup>-2</sup>.

Cell studies:

- 20 -

Electrochemical studies on lithium-ion half-cells were carried out in three-electrode Swagelok® cells using lithium metal foil (Rockwood Lithium, battery grade) as counter and reference electrodes. Accordingly, all the potential values given refer to the  $\text{Li/Li}^+$  reference couple. Glass microfiber (Whatman GF/D) was used as separator. Cells were assembled in an argon-filled MBraun glove box with a water and oxygen content of less than 0.5 ppm. Electrochemical studies were performed at  $20^\circ\text{C} \pm 2^\circ\text{C}$ . Galvanostatic cycling was performed by means of Maccor Battery Tester 4300.

SEM analysis:

*Ex situ* scanning electron microscope (SEM) analysis of aluminum current collectors (EVONIK, purity > 99.9%) was carried out on a ZEISS Auriga® microscope.

#### Example 4

Determination of anodic aluminum dissolution by LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2)

An electrolyte solution of 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) was prepared and cyclic voltammetry was performed by means of a VMP potentiostat/galvanostat, performing cyclic voltammetry using an aluminum disk of a diameter of 12 mm (Evonik, 99.99% purity) as working electrode. The sweep rate was set to  $5 \text{ mV s}^{-1}$ . The reversing potentials were set to 3.3 and 5.1 V vs  $\text{Li/Li}^+$  and the cell was polarized for 100 continuous cyclic sweeps. Subsequently, the cycled Swagelok® cells were disassembled in an MBraun dry box under argon. The polarized Al foils were rinsed with dimethyl carbonate (DMC), dried under vacuum, and transferred to a high resolution scanning electron microscope (HRSEM, ZEISS Auriga® microscope), using a modified sample holder to avoid contact to air and moisture.

Figure 1 shows the cyclic voltammogram for 1M LiTFSI in F-C2 for 100 cycles. As can be taken from the figure 1, after the first cycle the observed current density decreased significantly and almost no current was observed subsequently upon the second and the continuous potentiodynamic sweeps. No signs of anodic aluminum dissolution were detectable by performing the cyclic voltammetry. Also a subsequent SEM analysis of the aluminum foil polarized by the cyclic voltammetry in F-C2

comprising 1M LiTFSI did not show any indication of anodic aluminum dissolution and confirmed the prevention of aluminum dissolution. It is assumed that 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) initially formed a protective surface film of  $\text{AlF}_3$  on the aluminum surface and a thus prevented anodic aluminum dissolution of the aluminum foil upon further polarization.

5

#### Example 5

Electrochemical cell studies of an NMC half-cell using LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2)

10 An electrolyte solution of 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) was prepared and electrochemical cell studies were performed as described above. The cut-off potentials were at 3.0 and 4.3 V vs.  $\text{Li/Li}^+$ .

15 Figure 2 shows the corresponding potential profiles of the NMC half cell for the cycles 15, 20, 25, 30 and 35 at C/5 using F-C2 as electrolyte solvent. As can be taken from the figure 2, the potential profile was well preserved using F-C2 as the electrolyte solvent.

#### Comparative Example 6

20 Determination of anodic aluminum dissolution by LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1)

An electrolyte solution of 1M LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1) was prepared and cyclic voltammetry was performed by means of a VMP potentiostat/galvanostat, performing cyclic voltammetry using an aluminum disk of a diameter of 12 mm (Evonik, 99.99% purity) as working electrode. The sweep rate was set to  $5 \text{ mV s}^{-1}$ . The reversing potentials were set to 3.3 and 5.1 V vs  $\text{Li/Li}^+$  and the cell was polarized for 100 continuous cyclic sweeps. Subsequently, the cycled Swagelok<sup>®</sup> cells were disassembled in an MBraun dry box under argon. The polarized Al foils were rinsed with dimethyl carbonate (DMC), dried under vacuum, and transferred to a high resolution scanning electron microscope (HRSEM, ZEISS Auriga<sup>®</sup> microscope), using a modified sample holder to avoid contact to air and moisture.

30

- 22 -

Figure 3 shows the cyclic voltammogram for 1M LiTFSI in F-C1 as electrolyte solvent for 100 cycles. As can be taken from the figure 3, the cyclic voltammetry of F-C1-based electrolyte using lithium metal as counter and reference electrode and blank aluminum foil as working electrode showed severe anodic aluminum dissolution detectable by performing the cyclic voltammetry. Also a subsequent SEM analysis of the aluminum current collector showed severe corrosion of the anodic aluminum foil polarized by the cyclic voltammetry in F-C1. This shows that the lesser fluorinated carbamate N,N-dimethyl trifluoroethyl carbamate (F-C1) did not prevent aluminium corrosion.

#### 10 Comparative Example 7

Electrochemical cell studies of an NMC half-cell using LiTFSI in 1 N,N-dimethyl trifluoroethyl carbamate (F-C1)

15 An electrolyte solution of 1M LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1) was prepared and an electrochemical cell studies was performed as described above. The cut-off potentials were at 3.0 and 4.3 V vs. Li/Li<sup>+</sup>.

Figure 4 shows the corresponding potential profiles of the NMC half-cell for the cycles 15, 20, 25, 30 and 35 at C/5 using F-C1 as electrolyte solvent. As can be taken from the figure 4, the obtainable specific capacity is substantially decreasing upon cycling, indicated by the shortening of the corresponding potential profiles.

Figure 5 shows a comparison of the galvanostatic cycling of the Li/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC)-based cathode in half-cell configuration with Li as reference electrode and 1M LiTFSI in N,N-dimethyl trifluoroethyl carbamate (F-C1) or in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) as electrolytes as described in example 5 and the comparative example 7. It can be seen in the figure 5 that the NMC half-cells using the F-C1-based electrolytes show rapid capacity fading, while NMC half-cells using the F-C2-based electrolytes showed a stable cycling performance.

#### 30 Example 8

Determination of anodic aluminum dissolution by LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4)

An electrolyte solution of 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) was prepared and cyclic voltammetry was performed by means of a VMP potentiostat/galvanostat, performing cyclic voltammetry using an aluminum disk of a diameter of 12 mm (Evonik, 99.99% purity) as working electrode. The sweep rate was set to  $5 \text{ mV s}^{-1}$ . The cell was polarized for 100 continuous cyclic sweeps. Subsequently, the cycled cells were disassembled and the polarized Al foils were rinsed with dimethyl carbonate, dried, and transferred to a high resolution scanning electron microscope (HRSEM, ZEISS Auriga<sup>®</sup>).

Figure 6 shows the cyclic voltammogram for 1M LiTFSI in F-C4 as solvent for 100 cycles. Figure 1 shows that also for F-C4 the observed current density decreased significantly after the first cycle and almost no current was observed subsequently upon the second and the continuous potentiodynamic sweeps. Also the subsequent SEM analysis of the aluminum foil polarized by performing cyclic voltammetry confirmed that no aluminum corrosion was detectable. This shows that also 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) prevented anodic aluminum dissolution of the aluminum foil.

#### Example 9

Electrochemical cell studies of NMC half-cells using LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4)

An electrolyte solution of 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) was prepared and electrochemical cell studies were performed as described above. The cut-off potentials were set to 3.0 and 4.3 V vs.  $\text{Li/Li}^+$ .

Figure 7 shows the galvanostatic cycling of the NMC-based cathodes in half-cell configuration using 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte. It can be seen

- 24 -

in figure 7 that also the NMC half-cells comprising F-C4-based electrolytes showed stable cycling performance.

Figure 8 shows the corresponding potential profiles of the NMC half cell for the cycles 15, 20, 25, 30 and 35 at C/5 using F-C4 as electrolyte solvent. As can be taken from figure 8, the potential profile was well preserved using F-C4 as electrolyte solvent.

The examples 4 to 9 show that 1,1,1,3,3,3-hexafluoropropan-2-yl dimethyl and diethyl carbamate can be readily used for lithium-ion cells and are sufficiently stable towards oxidation, delivering the typical specific capacities for NMC-based cathodes in half-cell configuration, high cycling stability, and the characteristic electrochemical performance for such cathodes. These data indicate that the fluorinated carbamates appear as a promising electrolyte solvent for high voltage cathode materials such as NMC after a first activation cycle.

#### Example 10

Determination of different amounts of fluorinated carbamate as electrolyte solvent

The effect of different amounts of the fluorinated carbamate as electrolyte solvent for LiTFSI in regard of the prevention of aluminum current collector corrosion was investigated. Electrolyte solutions of 1M LiTFSI in the state-of-the-art carbonate solvent mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) in a weight ratio of 1:1 containing 33 wt%, 50 wt% or 80 wt%, respectively, of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) were prepared by adding F-C2 in a ratio of 1:1:1, 2:1:1 or 8:1:1, respectively, to EC/DMC (1:1).

Cyclic voltammetry was performed by means of a VMP potentiostat/galvanostat. For these studies, an aluminum disk of a diameter of 12 mm (Evonik, 99.99% purity) was used as working electrode with lithium metal as counter- and reference-electrode. The sweep rate was set to  $5 \text{ mV s}^{-1}$ . The reversing potentials were set to 3.3 and 5.1 V vs Li/Li<sup>+</sup> and the cell was polarized for 100 continuous cyclic sweeps. Subsequently, the cycled cells were disassembled, and the polarized aluminum foils were rinsed, dried and transferred to a high resolution scanning electron microscope.

- 25 -

Figures 9a), 9b) and 9c), respectively, show the cyclovoltammograms for 1M LiTFSI in 33 wt%, 50 wt% or 80 wt% of 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) in a 1:1 mixture of EC/DMC for 100 cycles using aluminum as working electrode. Figure 9a) shows a continuously increasing evolving current density during the continuous potentiodynamic sweeps. Within the first 5 cyclic sweeps a current density of up to  $3 \text{ mA cm}^{-2}$  was detected, indicating a severe anodic dissolution of the aluminum current collector, i.e., its corrosion as confirmed by massive pitting corrosion was observed by subsequent SEM analysis of the aluminum electrode. This illustrates that 33 wt% F-C2 as electrolyte solvent using LiTFSI as salt is not sufficient to avoid detrimental anodic aluminum dissolution of the current collector. The Figure 9b) shows that 50 wt% F-C2 resulted in significantly decreased current densities. However, for the first 20 cycles a current density of about  $0.5 \text{ mA cm}^{-2}$  was still detected and a massive pitting corrosion at the aluminum surface was observed by subsequent SEM analysis. The cyclic voltammogram given in Figure 9c) illustrates further decreased current densities to about  $0.1 \text{ mA cm}^{-2}$  using 80 wt% F-C2 as electrolyte solvent. A suppression of the detrimental aluminum dissolution in the first 10 polarization cycles was observed, indicated by the continuously decreasing current density upon these cyclic sweeps and confirmed by subsequent SEM analysis. The cyclic voltammograms presented in Figure 9 hence illustrate that about 80 wt% of the fluorinated carbamate according to the invention provide an effective aluminum passivation with respect to the occurring current within the initial cycles and substantially reduced the aluminum current collector corrosion.

#### Example 11

##### Determination of the electrochemical stability towards oxidation

The electrochemical stability towards oxidation was investigated by means of cyclic voltammetry (CV), performed at ambient temperature in an argon-filled glove box. A Pt wire and a Pt electrode with a diameter of 2 mm were utilized as counter and working electrode, respectively, and a sweep rate of  $2 \text{ mV s}^{-1}$  was applied. The reference electrode was an Ag wire in a 10mM solution of  $\text{AgNO}_3$  dissolved in acetonitrile including also 0.1M tetrabutylammonium tetrafluoroborate. The recorded potential can be converted to the NHE scale by adding 0.542 V and further converted to the potential

- 26 -

vs.  $\text{Li/Li}^+$ . The anodic stability limit was defined as the potential at which the current density is equal to  $0.1 \text{ mA cm}^{-2}$ .

Figure 10 shows the anodic stabilities using 1M LiTFSI in 1 N,N-dimethylethyl carbamate (C1), N,N-  
5 dimethyl trifluoroethyl carbamate (F-C1), 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2), or 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4) as electrolyte. It can be seen in figure 10 that the stability of the compounds F-C2 and F-C4 is increased compared to F-C1 and particularly to the non-fluorinated compound C1. This confirms that the presence of fluorine substituents have a beneficial impact on the electrochemical stability towards oxidation. The enhanced  
10 stability of C-F2 and C-F4 compared to C1 and C-F1 towards oxidation is assumed to be caused by the electron-withdrawing effect of the fluorine substituents, decreasing the electron donicity of the nitrogen atom.

Apart from properties as high thermal stability and ionic conductivity, the electrochemical stability is  
15 one of the most important characteristics for new electrolyte compositions, targeting the combination with high-voltage lithium-ion cathode materials. The determined values for the fluorinated carbamates appear sufficient for application as lithium-ion battery electrolyte in combination with state-of-the-art cathode materials like, for instance,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ .

## 20 Example 12

### Determination of anodic aluminum dissolution

In order to confirm the formation of a protective aluminum fluoride layer X-ray photoelectron spectroscopy (XPS), i.e., a surface sensitive analytical method was performed. X-ray photoelectron  
25 spectroscopy (XPS) was performed on aluminum foils which were potentiodynamically polarized for 10 cyclic sweeps in 1M LiTFSI in F-C2 and F-C4, utilizing an Axis Ultra HAS spectroscope (Kratos, GB) and a mono-chromatic Al  $K\alpha$  source (10 mA, 12 kV). Also for the XPS analysis, the samples were transferred to the instrument using a self-designed sample holder to avoid any contact to air and moisture. Measurements were carried out at a pass energy of 40 eV, using a charge neutralizer. The  
30 analyzed sample surface area was about  $100 \mu\text{m} \times 100 \mu\text{m}$ .  $\text{Ar}^+$  etching was carried out for 1 min at

0.5 kV and 8 mA for the first 10 times and subsequently twice for 1 min at 5 kV and 8 mA to obtain the herein presented depth profiling. All spectra were calibrated to 72.9 eV, referring to the Al 2p peak of metallic aluminum.

5 Figure 11 shows the results of the XPS analysis, panels (a) and (b) for 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate (F-C2) as electrolyte, and (c) and (d) for 1M LiTFSI in 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate (F-C4). The panels (a) and (c) show the recorded Al 2p XPS spectra, panels (b) and (d) the corresponding evolution of the atomic concentration upon etching ( $\text{AlF}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_{\text{metal}}$ , and C), respectively.

10

Referring to the Al 2p XPS spectra, as indicated by the characteristic binding energy, oxygen and fluorine are present in the form of  $\text{Al}_2\text{O}_3$  (O 1s; 532.0 eV) and  $\text{AlF}_3$  (F 1s; 686.6 eV), respectively.

This was further confirmed by the characteristic features in the Al 2p spectrum, occurring at 75.5 eV for  $\text{Al}_2\text{O}_3$  and 76.3 eV for  $\text{AlF}_3$ . Besides, metallic aluminum was detected at 72.9 eV. As can be seen

15 in the corresponding Al 2p spectra in Figure 11(a) and 11(c), for the electrolyte compositions based on F-C2 and F-C4, substantially increased amounts of aluminum fluoride were detected in addition to aluminum oxide. Also carbonaceous species were present at the current collector surface.

Nevertheless, their atomic concentration vanished immediately upon  $\text{Ar}^+$  etching as can be seen Figure 11(b) and 11(d). It is assumed that this carbon is a solvent-independent surface contamination. Upon

20 further  $\text{Ar}^+$  etching the fluorine peak, corresponding to  $\text{AlF}_3$ , decreased while growing metallic aluminum concentrations are observed.  $\text{Al}_2\text{O}_3$ , indicated by the O 1s feature, is also seen to decrease but only upon prolonged  $\text{Ar}^+$  etching, indicating that a thin layer of  $\text{AlF}_3$  is superposing that of  $\text{Al}_2\text{O}_3$ .

A comparison to aluminum foil polarized in 1M LiTFSI in the compound F-C1 showed that basically 25 oxygen and metallic aluminum were detected on the surface and a minor amount of fluorine.

However, only a very slight amount of aluminum fluoride was detected which appears insufficient for protecting the aluminum current collector from anodic dissolution.

Computing the thickness of the  $\text{AlF}_3$  layers using the XPS MultiQuant software revealed a thickness 30 of about only 0.7 nm for F-C1 and increased thicknesses for F-C2 of *ca.* 3.5 nm and F-C4 of *ca.* 1.4

- 28 -

nm. Obviously, the very thin layer in case of F-C1 is not sufficient to passivate the aluminum surface, while a thickness of 1.4 nm as in case of F-C4 appears to successfully prevent the anodic aluminum dissolution upon potentiodynamic polarization. In fact, the different layer thicknesses agree very well with the different current densities detected within the first voltammetric cycle with the two solvents.

- 5 The formation of a thicker  $\text{AlF}_3$  surface layer in case of F-C2 involves a more extensive oxidative solvent decomposition, i.e., a higher current, than in case of F-C4. This is also in line with the higher electrochemical stability of F-C4 compared to F-C2.

10 These data confirm that the fluorinated carbamates of the invention appear as a promising electrolyte solvent for high voltage cathode materials.

The work leading to this invention has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 29100329 AMELIE.

## CLAIMS

1. An electrolyte solution comprising an electrolyte salt and an electrolyte solvent, wherein the electrolyte solvent comprises at least one fluorinated carbamate according to the general formula (1)
 

5  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the provision that when one of  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is H or a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

10  $R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $C_1$ - $C_3$ -alkyl and the ring carbon atoms being optionally substituted with  $C_1$ - $C_3$ -alkyl, wherein said heterocycle or  $C_1$ - $C_3$ -alkyl groups are optionally substituted by at least one fluorine atom;

15  $R^3$  is selected from the group comprising H, F, CN, perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl, and

wherein the electrolyte solvent comprises the fluorinated carbamate in an amount in the range from  $\geq$

20 80 wt% to  $\leq$  100 wt%, referring to a total amount of the electrolyte solvent of 100 wt%, and

wherein the electrolyte salt is selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of  $-CF_3$  and  $-CN$ -substituted Hückel-anions, secondary carbanions substituted by  $(CF_3SO_2)_2CH^-$ , tertiary carbanions substituted by  $(CF_3SO_2)_3C^-$ ,  $(N\equiv C)_3C^-$  or  $(FSO_2)_3C^-$ , pentacyano

25 cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $SO_3^-$ -end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts.
  2. The electrolyte solution according to claim 1, wherein  $R^3$  is selected from the group comprising H, F and/or perfluorinated linear  $C_1$ - $C_3$ -alkyl, preferably  $R^3$  is selected from the group
- 30 comprising H, F,  $CF_3$  and/or  $C_2F_5$ .

- 30 -

3. The electrolyte solution according to claim 1 or 2, wherein  $R^4$  and  $R^5$  are the same or independently of the other perfluorinated linear  $C_1$ - $C_3$ -alkyl, preferably selected from the group comprising  $CF_3$  and/or  $C_2F_5$ .

5

4. The electrolyte solution according to any of the preceding claims, wherein  $R^1$  and  $R^2$  are selected, the same or independently of the other, from the group comprising linear or branched  $C_1$ - $C_3$ -alkyl, preferably selected from the group comprising methyl and/or ethyl.

10

5. The electrolyte solution according to any of the preceding claims, wherein the fluorinated carbamate is selected from the group comprising 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate, 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate, and mixtures thereof.

15

6. The electrolyte solution according to any of the preceding claims, wherein the electrolyte solution comprises the fluorinated carbamate in a range from  $\geq 85$  wt% to  $\leq 100$  wt%, preferably in a range of  $\geq 90$  wt% to  $\leq 100$  wt%, more preferably in a range of  $\geq 95$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%.

20

7. The electrolyte solution according to any of the preceding claims, wherein the electrolyte solution comprises at least one non-fluorinated organic carbonate selected from the group comprising ethylene carbonate, ethyl methyl carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and mixtures thereof.

25

8. The electrolyte solution according to any of the preceding claims, wherein the alkali or alkaline earth metal sulfonimide or sulfonate salt is a lithium salt selected from the group comprising lithium bis(trifluoromethanesulfonyl)imide, lithium bis(fluorosulfonyl)imide, lithium (trifluoromethylsulfonyl)(nonafluorobutanesulfonyl)imide, lithium (fluorosulfonyl)(nonafluorobutanesulfonyl)imide, lithium (nonafluoro butan-2-one sulfonyl)(trifluoromethylsulfonyl)imide, lithium (nonafluoro butan-2-one sulfonyl)(fluorosulfonyl)imide and/or lithium trifluoromethanesulfonate.

30

9. An alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device, particularly a lithium battery, a primary or secondary lithium-ion battery, a lithium polymer battery or a lithium-ion capacitor, comprising an electrolyte solution according to any  
5 of the preceding claims.

10. A method for preventing aluminum current collector corrosion in an alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device containing an electrolyte solution comprising an electrolyte salt and an electrolyte solvent, the method comprising  
10 the step of using an electrolyte solvent comprising in a range from  $\geq 80$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%, of at least one fluorinated carbamate according to the general formula (1)  $R^1R^2NC(O)OCR^3R^4R^5$  wherein:

$R^1, R^2$  are selected, the same or independently of the other, from the group comprising H, linear  $C_1$ - $C_4$ -alkyl, branched  $C_3$ - $C_4$ -alkyl and/or  $C_3$ - $C_7$ -cycloalkyl, with the provision that when one of  
15  $R^1$  or  $R^2$  is  $C_3$ - $C_7$ -cycloalkyl the other is H or a  $C_1$ - $C_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

$R^1$  and  $R^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $C_1$ -  
20  $C_3$ -alkyl and the ring carbon atoms being optionally substituted with  $C_1$ - $C_3$ -alkyl, wherein said heterocycle or  $C_1$ - $C_3$ -alkyl groups are optionally substituted by at least one fluorine atom;

$R^3$  is selected from the group comprising H, F, CN, perfluorinated linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl;

$R^4, R^5$  are selected, the same or independently of the other, from the group comprising perfluorinated  
25 linear  $C_1$ - $C_4$ -alkyl and/or perfluorinated branched  $C_3$ - $C_4$ -alkyl, and

wherein the electrolyte salt is selected from the group comprising alkali metal or alkaline earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of  $-CF_3$  and  $-CN$ -substituted Hückel-anions, secondary carbanions substituted by  $(CF_3SO_2)_2CH^-$ , tertiary carbanions substituted by  $(CF_3SO_2)_3C^-$ ,  $(N\equiv C)_3C^-$  or  $(FSO_2)_3C^-$ , pentacyano

- 32 -

cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions,  $\text{SO}_3^-$ -end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts.

11. The method according to claim 10, wherein  $\text{R}^3$  is selected from the group comprising H, F and/or perfluorinated linear  $\text{C}_1$ - $\text{C}_3$ -alkyl, preferably  $\text{R}^3$  is selected from the group comprising H, F,  $\text{CF}_3$  and/or  $\text{C}_2\text{F}_5$ .

12. The method according to claims 10 or 11, wherein  $\text{R}^4$  and  $\text{R}^5$  are the same or independently of the other perfluorinated linear  $\text{C}_1$ - $\text{C}_3$ -alkyl, preferably selected from the group comprising  $\text{CF}_3$  and/or  $\text{C}_2\text{F}_5$ .

13. The method according to claims 10 to 12, wherein the fluorinated carbamate is selected from the group comprising 1,1,1,3,3,3-hexafluoropropan-2-yl dimethylcarbamate, 1,1,1,3,3,3-hexafluoropropan-2-yl diethylcarbamate, and mixtures thereof.

14. The method according to claims 10 to 13, wherein the electrolyte solution comprises the fluorinated carbamate in a range from  $\geq 85$  wt% to  $\leq 100$  wt%, preferably in a range of  $\geq 90$  wt% to  $\leq 100$  wt%, more preferably in a range of  $\geq 95$  wt% to  $\leq 100$  wt%, referring to a total amount of the electrolyte solvent of 100 wt%.

15. Use of a fluorinated carbamate according to the general formula (1)  $\text{R}^1\text{R}^2\text{NC}(\text{O})\text{OCR}^3\text{R}^4\text{R}^5$  wherein:

$\text{R}^1$ ,  $\text{R}^2$  are selected, the same or independently of the other, from the group comprising H, linear  $\text{C}_1$ - $\text{C}_4$ -alkyl, branched  $\text{C}_3$ - $\text{C}_4$ -alkyl and/or  $\text{C}_3$ - $\text{C}_7$ -cycloalkyl, with the provision that when one of  $\text{R}^1$  or  $\text{R}^2$  is  $\text{C}_3$ - $\text{C}_7$ -cycloalkyl the other is H or a  $\text{C}_1$ - $\text{C}_2$  alkyl group, wherein said alkyl or cycloalkyl groups are optionally substituted by at least one fluorine atom, or

$\text{R}^1$  and  $\text{R}^2$  directly or via one or more additional nitrogen and/or oxygen atoms are linked to form together with the nitrogen atom to which they are attached a 3- to 7-membered non aromatic heterocycle, wherein the additional nitrogen atoms present in the ring being saturated with  $\text{C}_1$ -

- 33 -

C<sub>3</sub>-alkyl and the ring carbon atoms being optionally substituted with C<sub>1</sub>-C<sub>3</sub>-alkyl, wherein said heterocycle or C<sub>1</sub>-C<sub>3</sub>-alkyl groups are optionally substituted by at least one fluorine atom;

R<sup>3</sup> is selected from the group comprising H, F, CN, perfluorinated linear C<sub>1</sub>-C<sub>4</sub>-alkyl and/or perfluorinated branched C<sub>3</sub>-C<sub>4</sub>-alkyl;

5 R<sup>4</sup>, R<sup>5</sup> are selected, the same or independently of the other, from the group comprising perfluorinated linear C<sub>1</sub>-C<sub>4</sub>-alkyl and/or perfluorinated branched C<sub>3</sub>-C<sub>4</sub>-alkyl,

for the prevention of aluminum current collector corrosion in an alkali metal or alkaline earth metal-based or an Al-based or Zn-based electrochemical energy storage device, containing an electrolyte solution comprising an electrolyte salt selected from the group comprising alkali metal or alkaline

10 earth metal, Al or Zn sulfonimide, methide, sulfonate or oxalatoborate salts, or alkali metal or alkaline earth metal, Al or Zn salts of -CF<sub>3</sub> and -CN-substituted Hückel-anions, secondary carbanions substituted by (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>CH<sup>-</sup>, tertiary carbanions substituted by (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, (N≡C)<sub>3</sub>C<sup>-</sup> or (FSO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, pentacyano cyclopentadienyl, arylsulfonyl, trifluoromethane sulfonyl amide anions, SO<sub>3</sub><sup>-</sup>-end-capped or sulfonamide end-capped polyethylene glycol, and mixtures of these salts, and an electrolyte solvent,

15 wherein the fluorinated carbamate is used in an amount in the range from ≥ 80 wt% to ≤ 100 wt%, referring to a total amount of the electrolyte solvent of 100 wt%.

1 / 7

Figure 1

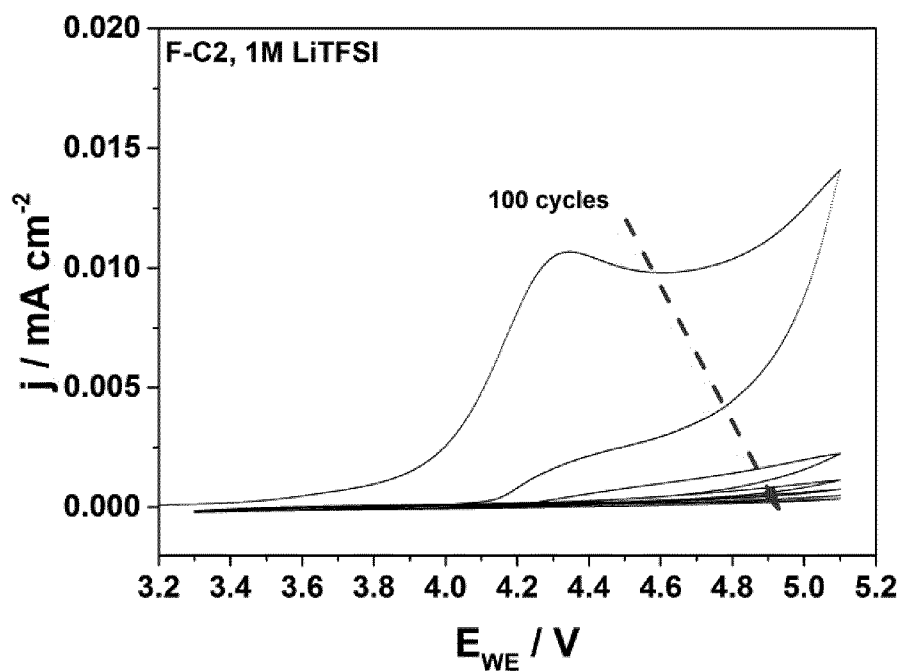
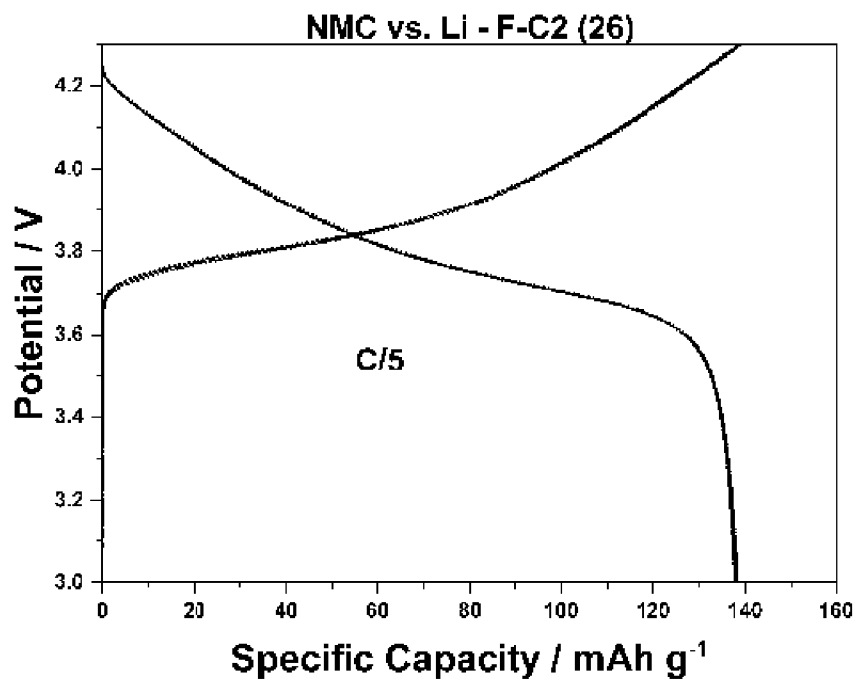


Figure 2



2 / 7

Figure 3

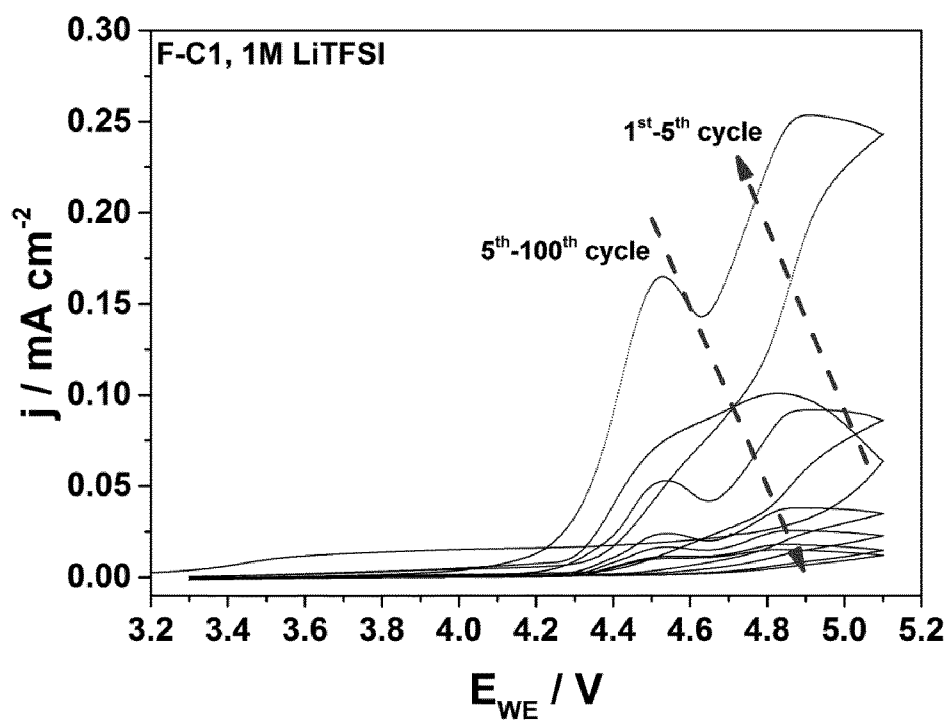
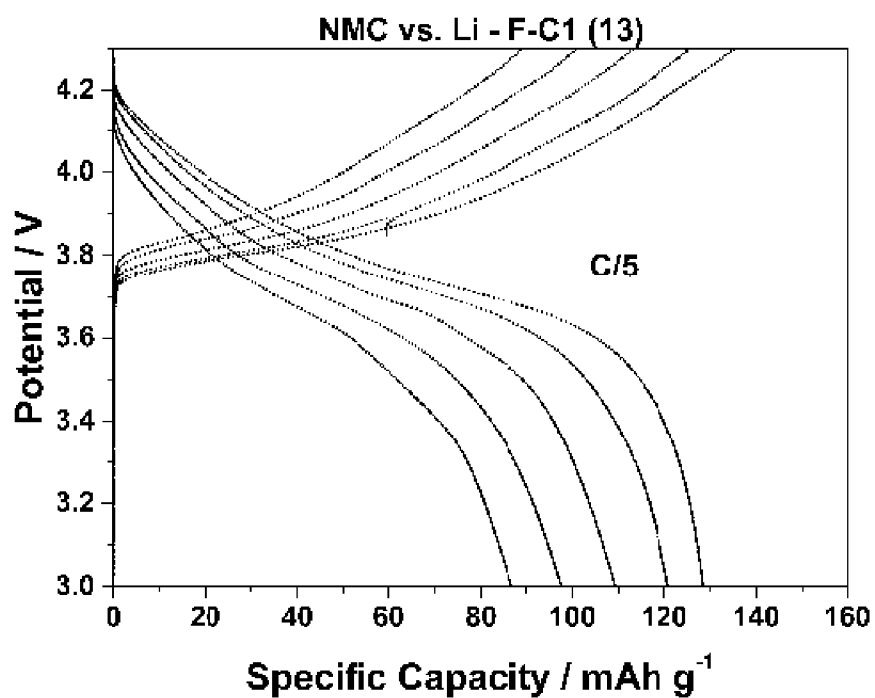


Figure 4



3 / 7

Figure 5

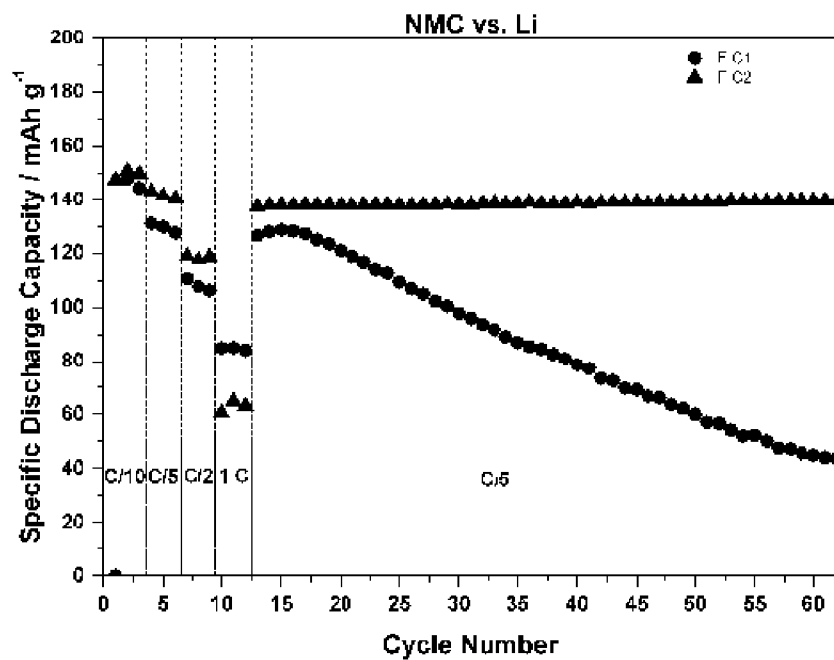
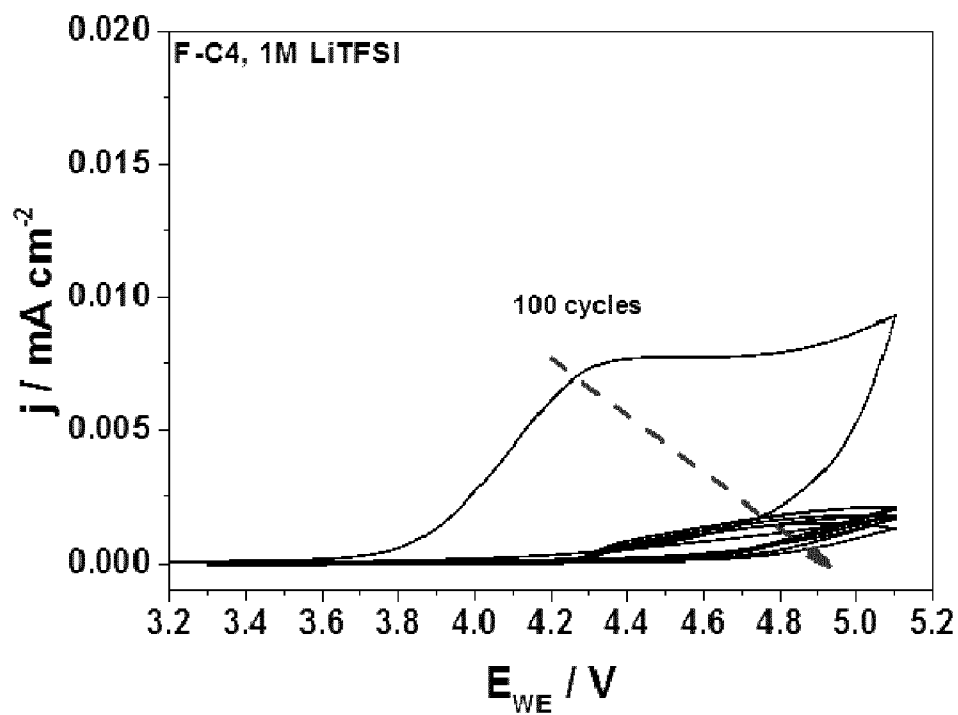


Figure 6



4 / 7

Figure 7

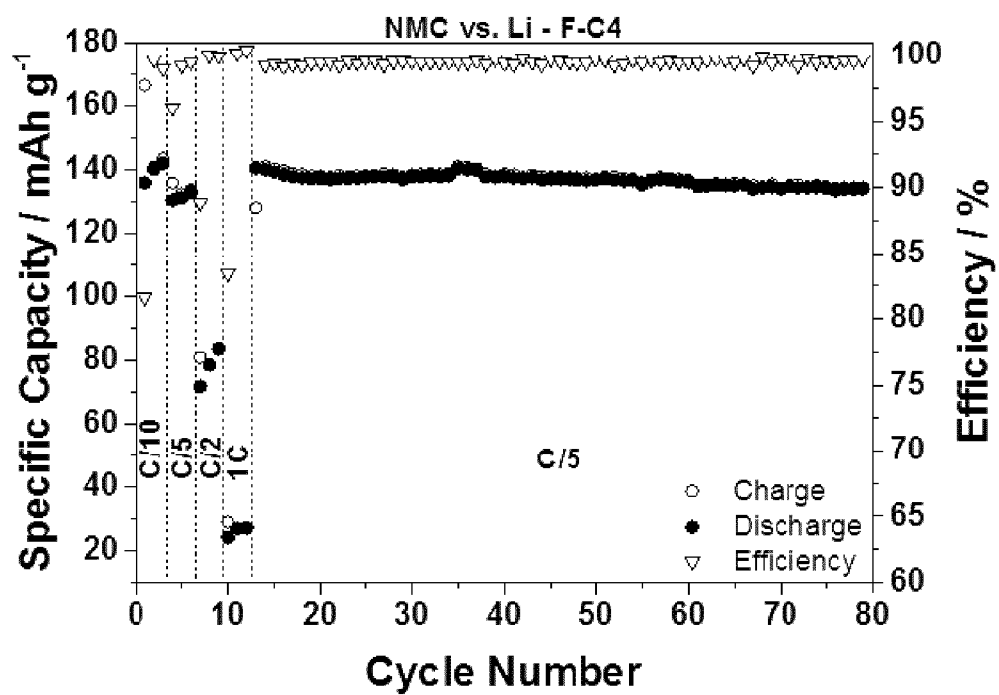
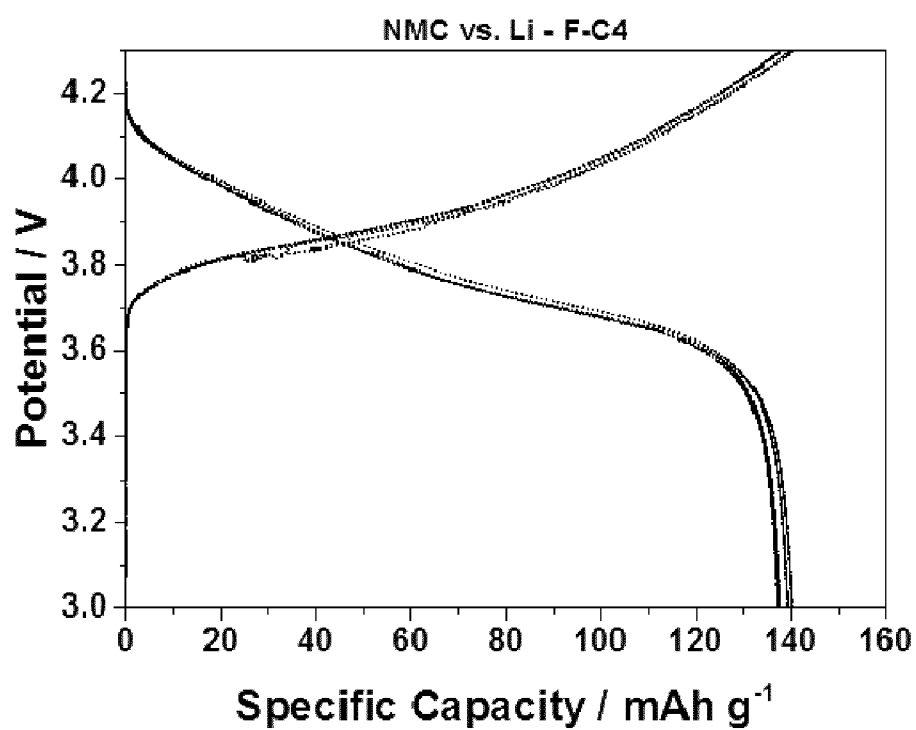


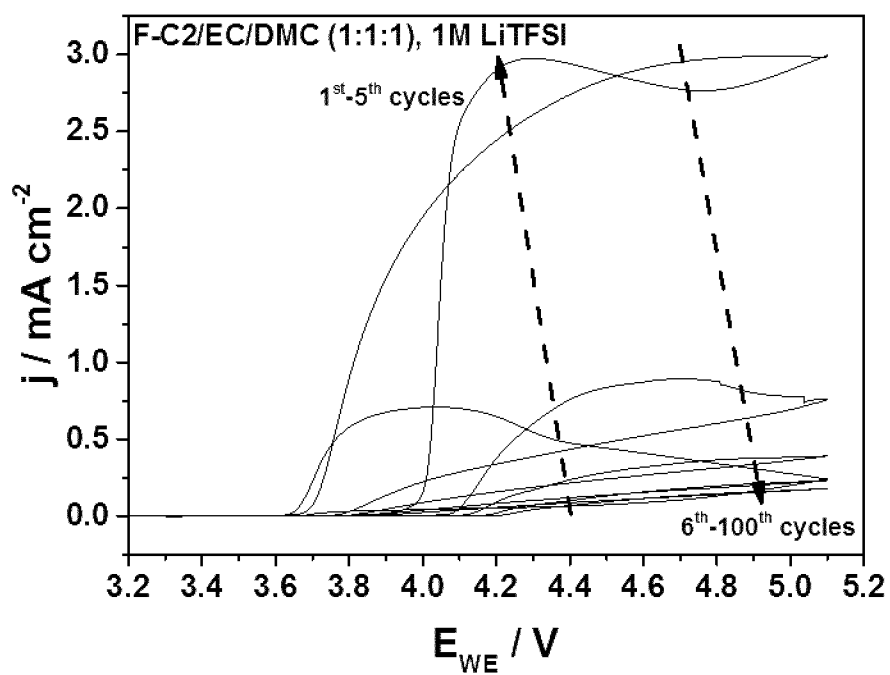
Figure 8



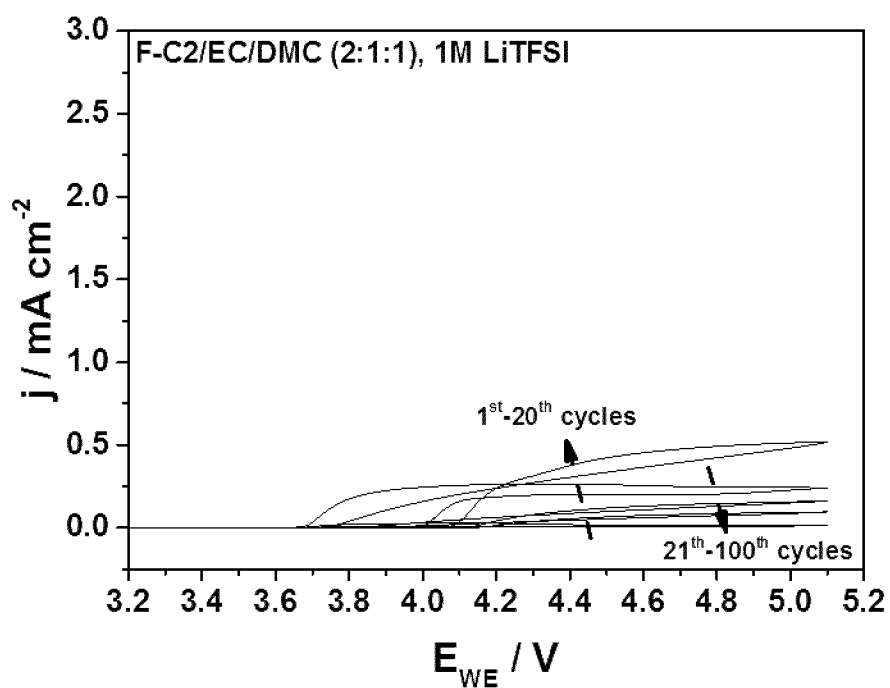
5 / 7

Figure 9

a)



b)



6/7

Figure 9

c)

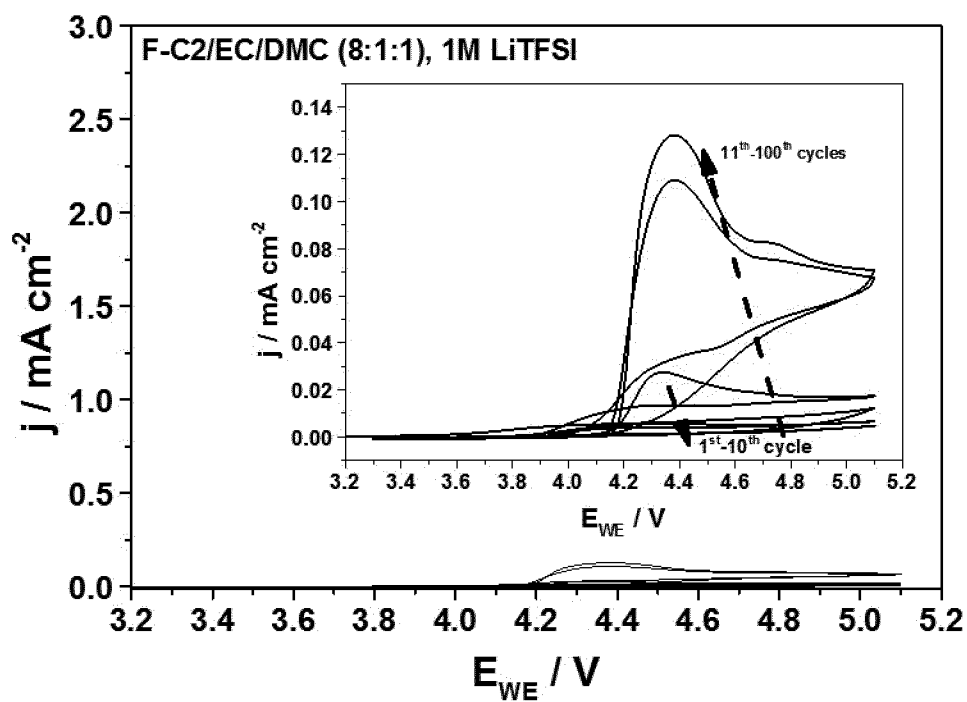


Figure 10

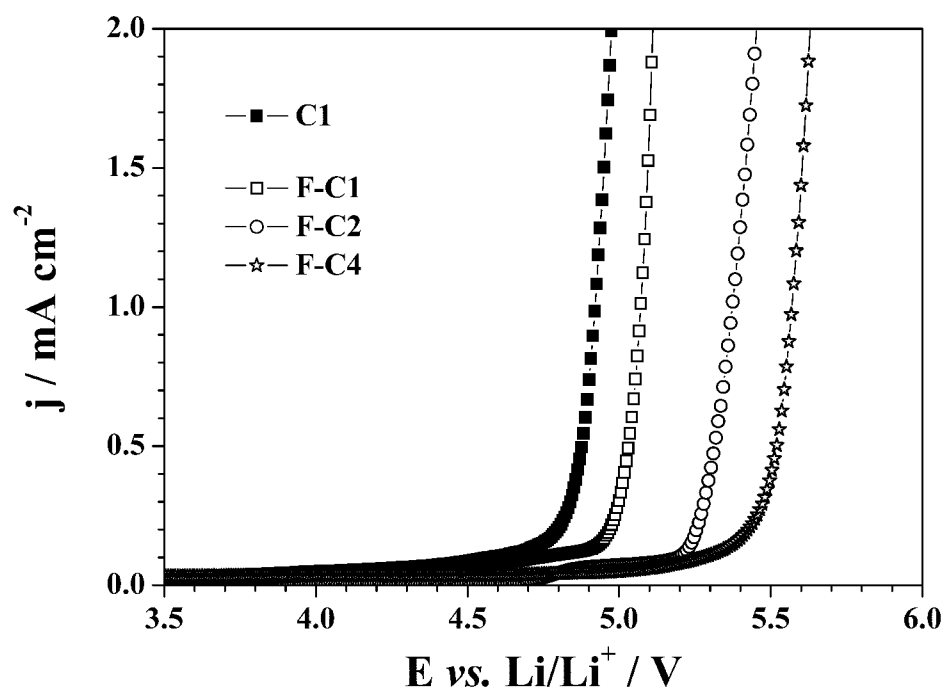
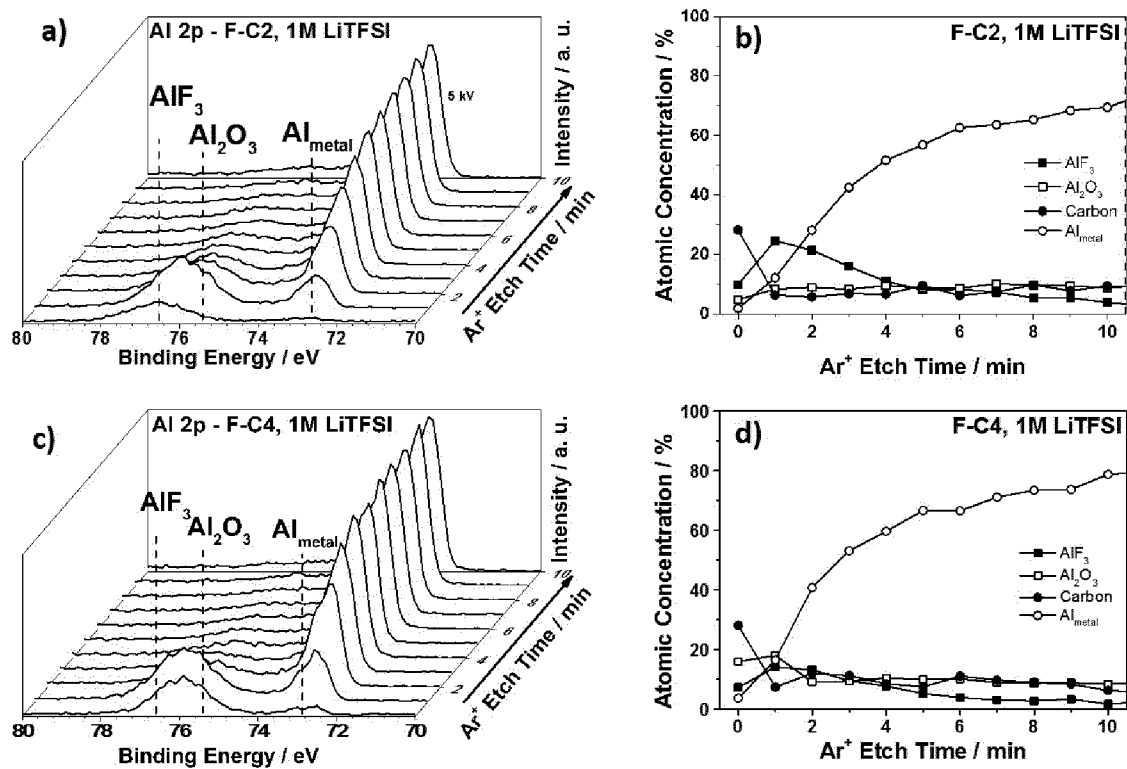


Figure 11



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/067564

A. CLASSIFICATION OF SUBJECT MATTER  
INV. H01M10/052 H01M10/0568 H01M10/0569 H01M6/16 H01M10/054  
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, CHEM ABS Data, 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         | US 6 159 640 A (APPEL WOLFGANG [DE] ET AL)<br>12 December 2000 (2000-12-12)<br>cited in the application<br>column 4, lines 50-52; claim 1<br>column 6, lines 33-34 | 1-15                  |
| A         | -----<br>US 2012/077091 A1 (LEE BYOUNG-BAE [KR] ET<br>AL) 29 March 2012 (2012-03-29)<br>claims 1-3                                                                 | 1-15                  |
| A         | -----<br>US 2013/164637 A1 (LEE BYOUNG BAE [KR] ET<br>AL) 27 June 2013 (2013-06-27)<br>claims 1-3<br>-----                                                         | 1-15                  |



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

21 September 2015

Date of mailing of the international search report

06/10/2015

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

Steinreiber, J

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/067564

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date         |
|-------------------------------------------|---------------------|----------------------------|-----------------------------|
| US 6159640                                | A                   | 12-12-2000                 | AT 482483 T 15-10-2010      |
|                                           |                     | CA 2240605 A1              | 13-12-1998                  |
|                                           |                     | DE 19724709 A1             | 17-12-1998                  |
|                                           |                     | EP 0887874 A2              | 30-12-1998                  |
|                                           |                     | JP 4383556 B2              | 16-12-2009                  |
|                                           |                     | JP H1197060 A              | 09-04-1999                  |
|                                           |                     | US 6159640 A               | 12-12-2000                  |
| -----                                     |                     |                            |                             |
| US 2012077091                             | A1                  | 29-03-2012                 | CN 102473961 A 23-05-2012   |
|                                           |                     |                            | EP 2525433 A2 21-11-2012    |
|                                           |                     |                            | KR 20110084131 A 21-07-2011 |
|                                           |                     |                            | US 2012077091 A1 29-03-2012 |
| -----                                     |                     |                            |                             |
| US 2013164637                             | A1                  | 27-06-2013                 | NONE                        |
| -----                                     |                     |                            |                             |