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(54) Title: FLAME-RETARDANT ELECTROLYTE COMPOSITION FOR LITHIUM-ION BATTERIES

(57) Abstract: This invention relates to electrolyte flame-retardant compositions for lithium ion batteries.



WO 2017/210593 A1

## FLAME-RETARDANT ELECTROLYTE COMPOSITION FOR LITHIUM-ION BATTERIES

### TECHNICAL FIELD

This invention relates to electrolyte flame-retardant compositions for lithium ion batteries.

### BACKGROUND

5 A lithium ion battery is a container comprising a positive electrode, a negative electrode and a separator (insulating layer) interposed between the positive electrode and the negative electrode. The battery also typically contains a non-aqueous electrolyte composition comprising a non-aqueous solvent with a lithium salt dissolved therein. Under a load, the electrolyte composition allows the positive charge lithium ions to migrate from the negative electrode through the  
10 separator to the positive electrode. For each lithium ion, an electron must make the same journey through an external circuit resulting in an electrical current.

The positive electrode active material is usually composed of a composite metal oxide, such as a lithium-containing transition metal oxide (e.g.,  $\text{LiCoO}_2$ ). The negative electrode is typically composed of a material capable of absorbing and desorbing lithium ions, for example, a carbon  
15 material such as graphite.

The separator is usually a microporous membrane made of a polyolefin resin such as polyethylene, polypropylene, polyethylene oxide, polyvinylidene fluoride or polyacrylate.

In the non-aqueous electrolyte composition, the lithium salt (e.g.,  $\text{LiPF}_6$ ) is dissolved in a non-aqueous solvent. The solvent used in the electrolyte should be able to dissolve the lithium salt,  
20 have low viscosity to allow the movement of the lithium ions and be stable at the electrodes. Typically, ethylene carbonate or dialkyl carbonates are used as the non-aqueous solvent.

However, due to relatively low flash or inflammation points of these non-aqueous solvents, the non-aqueous electrolyte composition may have fire safety or explosions problems. The problems would likely be caused by improper operations, such as short-circuiting, overcharging  
25 or over-discharging. To reduce these problems, it has been proposed to prepare non-aqueous

electrolyte compositions containing flame retardant additives. Typically, these flame retardant additives are phosphorus-containing flame retardants.

The present application relates, however, to brominated flame retardants, which may be used as additives for non-aqueous electrolyte compositions having improved results over traditional  
5 flame retardant additives used in lithium ion batteries.

### SUMMARY OF THE INVENTION

The present invention relates to an electrolyte flame-retardant compositions comprising: a) an organic solvent; b) a lithium salt; and c) a brominated flame retardant selected from the group consisting of tribromoneopentyl alcohol, dibromoneopentyl glycol, 2,4,6-(tris(2,4,6-  
10 tribromophenoxy)-1,3,5-triazine, tetrabromobiphenol, tetrabromobiphenol carbonate, tetrabromobiphenol epoxy, tetrabromobisphenol F, tetrabromobisphenol F carbonate, tetrabromobisphenol F epoxy, tetrabromobisphenol S, tetrabromobisphenol S carbonate, tetrabromobisphenol S epoxy, (tetrabromobiphenol-bis(2,3-dibromopropyl ether)), (tetrabromobiphenol-bis(2,3-dibromo-2-methylpropyl ether)), (tetrabromobisphenol F-bis(2,3-  
15 dibromopropyl ether)), (tetrabromobisphenol F-bis(2,3-dibromo-2-methylpropyl ether)), (tetrabromobisphenol S-bis(2,3-dibromopropyl ether)), (tetrabromobisphenol S-bis(2,3-dibromo-2-methylpropyl ether)), tribromophenol, dibromoethyldibromocyclohexane, tetrabromocyclooctane, bromopropanol, 2,3-dibromo-2-propen-1-ol, 2,3-dibromo-2-buten-1,4-diol,, pentabromobenzyl methacrylate, , 2,2',6,6'-Tetrabromobisphenol A diglycidyl ether,  
20 tribromoethylene, 1,3-dibromo-2,2-dimethylpropane, 2,2-bis(bromomethyl)-1,3-dibromopropane, lithium salts of the brominated flame retardant containing hydroxyl groups, or combinations thereof.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an electrolyte flame-retardant composition comprising: a) an  
25 organic solvent; b) a lithium salt; and c) a brominated flame retardant selected from the group consisting of the flame retardant components described above.

The lithium salt used in electrolyte flame-retardant compositions may be any lithium salt generally used in the art. For example, the lithium salt may be  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ ,  $\text{LiClO}_4$ ,  $\text{LiAlO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiAlF}_4$ ,  $\text{LiBPh}_4$ ,  $\text{LiB}_{10}\text{Cl}_{10}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ ,  $\text{C}_4\text{F}_3\text{SO}_3\text{Li}$ ,  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ ,  $\text{LiN}(\text{C}_x\text{F}_{2x+1}\text{SO}_2)(\text{C}_x\text{F}_{2y+1}\text{SO}_2)$  (wherein, x and y are whole positive numbers),  $\text{CF}_3\text{CO}_2\text{Li}$ ,  $\text{LiCl}$ ,  $\text{LiI}$ , lithium bis(oxalate) borate (LIBOB), a  $\text{C}_1$  to  $\text{C}_6$  aliphatic lithium carbonate, phenyl lithium borate, lithium imide, or combinations thereof.

The concentration of the lithium salt may be in a range of concentrations used in the art. For example, the lithium salt may be used at a concentration of about 0.1 molar (M) to about 2.5 M, or about 0.65M to about 2 M, or about 0.8 M to about 1.8 M, or about 0.9M to 1.5 M, but the concentrations are not limited thereto.

The organic solvent used in electrolyte flame-retardant compositions may be any organic solvent used in the art. The organic solvent may be a polar aprotic solvent such as a carbonate-based solvent, an ester-based solvent, an ether-based solvent, a ketone-based solvent, an alcohol-based solvent or combinations thereof.

In most lithium ion batteries, carbonate-based solvents are used. The carbonate-based solvents may be a chain carbonate compound, a cyclic carbonate compound, a fluorocarbonate compound or combinations thereof.

Non limiting examples of chain carbonate compounds may be, for example, diethyl carbonate, dimethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, methyl ethyl carbonate, or a combination thereof. Non limiting examples of cyclic carbonate compound may be, for example, ethylene carbonate, propylene carbonate, butylene carbonate, vinyl ethylene carbonate, or combinations thereof.

The fluorocarbonate compound may be, for example, fluoroethylene carbonate, 4,5-difluoroethylene carbonate, 4,4-difluoroethylene carbonate, 4,4,5-trifluoroethylene carbonate, 4,4,5,5-tetrafluoroethylene carbonate, 4-fluoro-5-methylethylene carbonate, 4-fluoro-4-methylethylene carbonate, 4,5-difluoro-4-methyl ethylene carbonate, 4,4,5-trifluoro-5-methylethylene carbonate, trifluoromethyl ethylene carbonate, or combinations thereof.

The carbonate-based solvents are typically used as mixtures of the cyclic carbonate and the chain carbonate compounds because the dielectric constant and viscosity of the mixtures are especially suitable for electrolyte compositions. For example, a volume ratio of the cyclic carbonate compound to the chain carbonate compound may be about 1:1 to about 1:9. The carbonate-based  
5 compound may have a fluorocarbonate compound further added to the mixture of the chain and/or cyclic carbonate compound. The fluorocarbonate compound may increase solubility of a lithium salt to increase ion conductivity and may facilitate formation of a film on the negative electrode.

Non-limiting examples of ester-based solvents that may be used are: methyl acetate, ethyl  
10 acetate, n-propyl acetate, dimethyl acetate, methyl propionate, ethyl propionate,  $\gamma$ -butyrolactone, decanolide, valerolactone, mevalonolactone, caprolactone, methyl formate, or combinations thereof.

Non-limiting examples of ether-based solvent, dibutyl ether, tetraglyme, diglyme, 1,2-dimethoxy ethane, 1,2-diethoxy ethane, ethoxy methoxy ethane, 2-methyl tetrahydrofuran, tetrahydrofuran,  
15 ("THF"), or combinations thereof.

Non-limiting examples of the ketone-based solvent, for example, cyclohexanone and examples of the alcohol-based solvent are: ethyl alcohol, isopropyl alcohol, or combinations thereof.

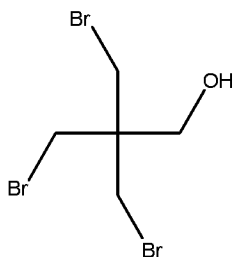
The non-aqueous organic solvent may be used alone or as a mixture of two or more thereof and when two or more thereof are used as a mixture, a mixture ratio may be suitably adjusted  
20 according to a desired battery performance and this may be easily understood by one of ordinary skill in the art.

The organic solvent may further include an aromatic hydrocarbon-based organic solvent in addition to the carbonate-based solvent. In this regard, the carbonate-based solvent and an aromatic hydrocarbon-based organic solvent may be mixed in a volume ratio of, for example,  
25 about 1:1 to about 30:1.

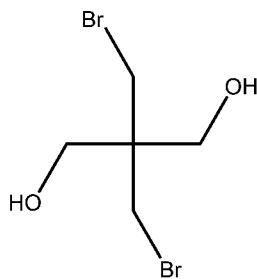
Non-limiting examples of the aromatic hydrocarbon-based organic solvent are: benzene, fluorobenzene, 1,2-difluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene, 1,2,3-

trifluorobenzene, 1,2,4-trifluorobenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, iodobenzene, 1,2-diiodobenzene, 1,3-diiodobenzene, 1,4-diiodobenzene, 1,2,3-triiodobenzene, 1,2,4-triiodobenzene, toluene, fluorotoluene, 1,2-difluorotoluene, 1,3-difluorotoluene, 1,4-difluorotoluene, 1,2,3-trifluorotoluene, 1,2,4-trifluorotoluene, chlorotoluene, 1,2-dichlorotoluene, 1,3-dichlorotoluene, 1,4-dichlorotoluene, 1,2,3-trichlorotoluene, 1,2,4-trichlorotoluene, iodotoluene, 1,2-diiodotoluene, 1,3-diiodotoluene, 1,4-diiodotoluene, 1,2,3-triiodotoluene, 1,2,4-triiodotoluene, xylene, or combinations thereof.

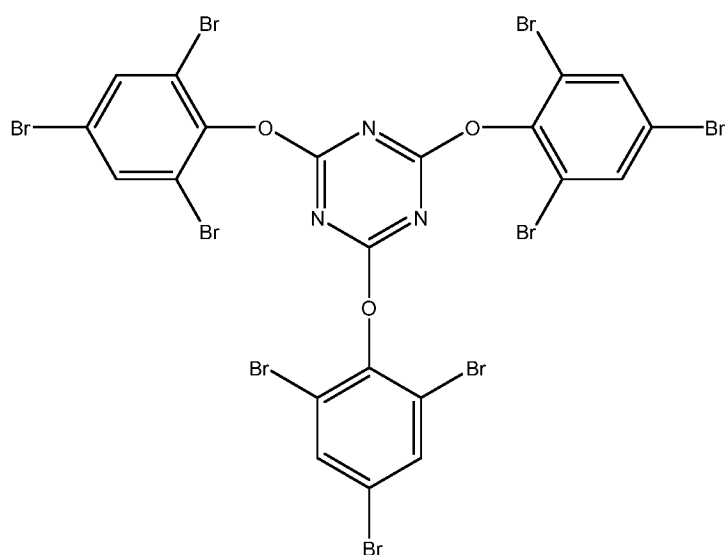
The brominated flame retardant may be selected from: tribromophenol, dibromoethyldibromocyclohexane, tetrabromocyclooctane, bromopropanol, tetrabromobisphenol A bis (allyl ether), 2,2',6,6'-Tetrabromobisphenol A diglycidyl ether, 2,3-dibromo-2-propen-1-ol, 2,3-dibromo-2-buten-1,4-diol, pentabromobenzyl acrylate, pentabromobenzyl methacrylate,



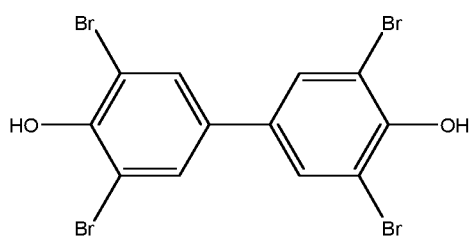
Tribromoneopentyl alcohol



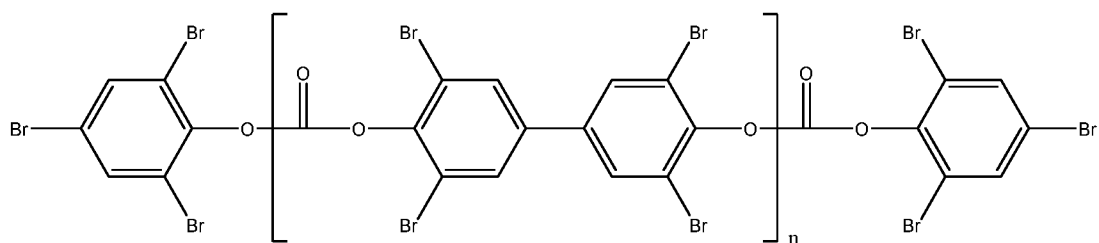
Dibromoneopentyl glycol



2,4,6-(tris(2,4,6-tribromophenoxy))-1,3,5-triazine

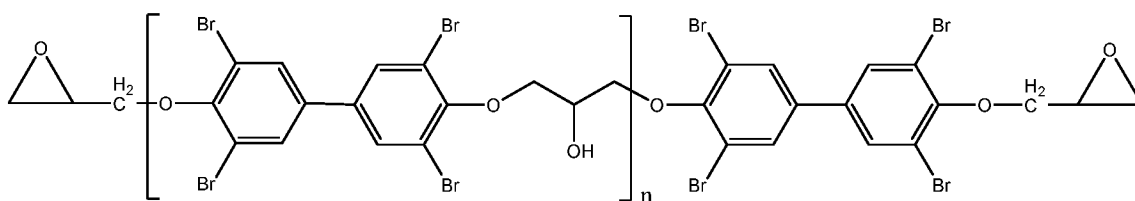


tetrabromobiphenol



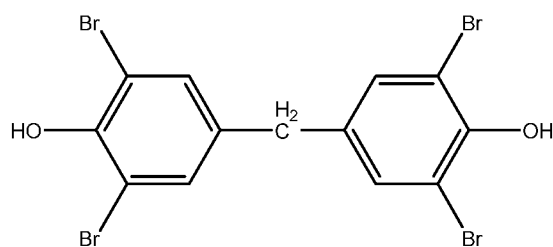
Tetrabromobiphenol carbonate

$$n = 1-10$$



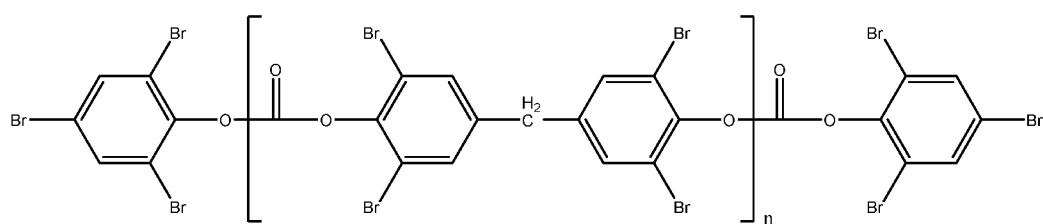
Tetrabromobiphenol epoxy

n = 0-10



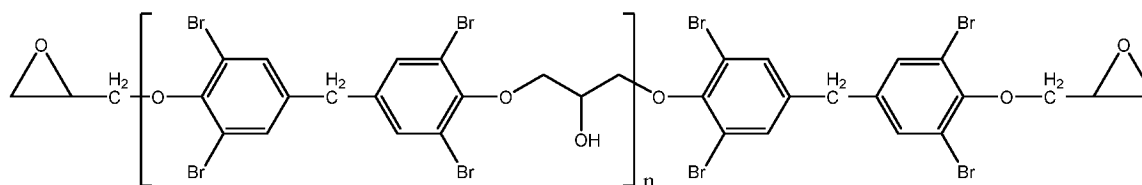
5

Tetrabromobisphenol F



Tetrabromobisphenol F carbonate

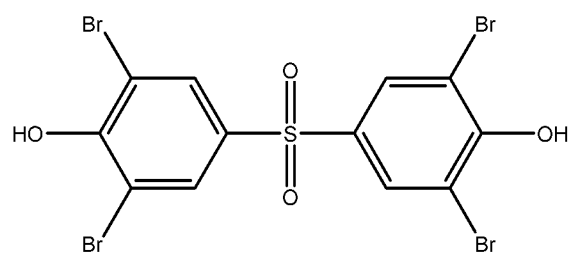
n = 1-10



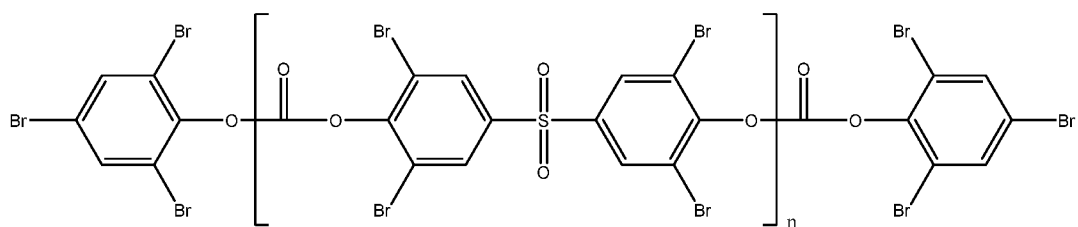
10

Tetrabromobisphenol F epoxy

n = 0-10

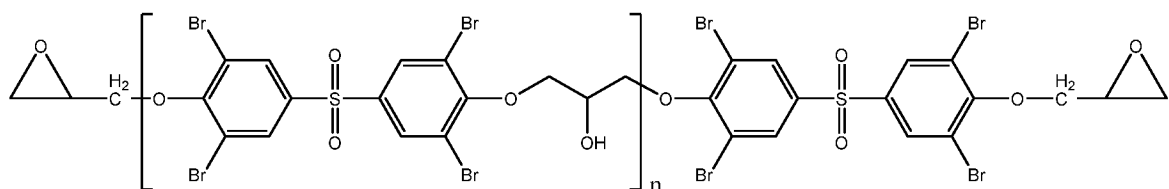


Tetrabromobisphenol S

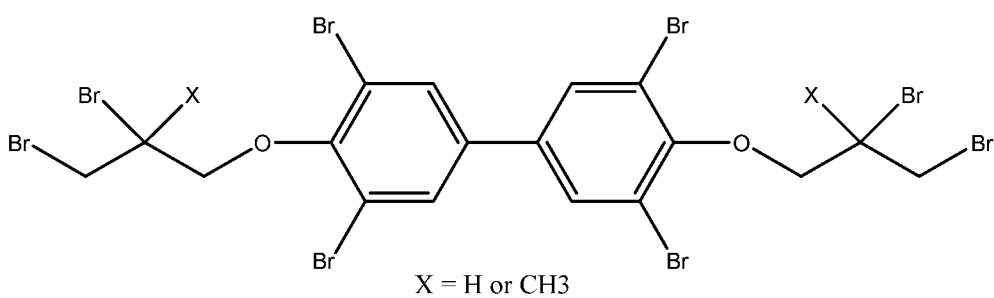


Tetrabromobisphenol S carbonate

5

 $n = 1-10$ 

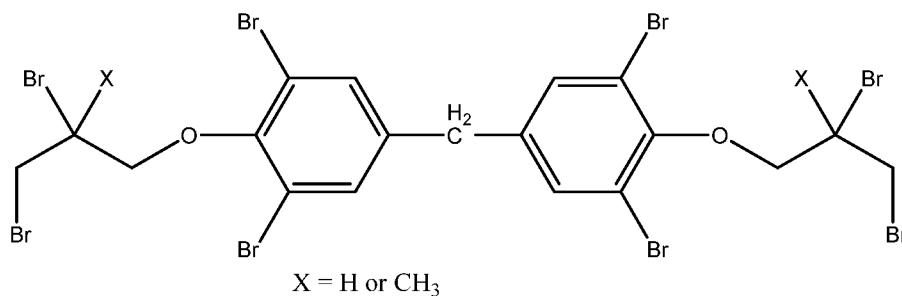
Tetrabromobisphenol S epoxy

 $n = 0-10$ 

10

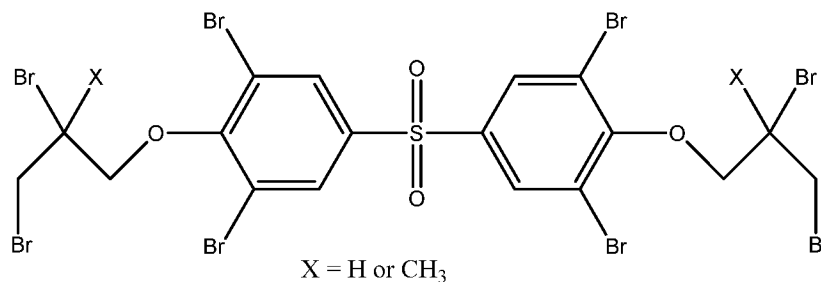
(tetrabromobiphenol-bis(2,3-dibromopropyl ether)) (X=H)

(tetrabromobiphenol-bis(2,3-dibromo-2-methylpropyl ether)) (X=CH<sub>3</sub>)



(tetrabromobisphenol F-bis(2,3-dibromopropyl ether)) (X=H)

5 (tetrabromobisphenol F-bis(2,3-dibromo-2-methylpropyl ether)) (X=CH<sub>3</sub>)



(tetrabromobisphenol S-bis(2,3-dibromopropyl ether)) (X=H),

(tetrabromobisphenol S-bis(2,3-dibromo-2-methylpropyl ether)) (X=CH<sub>3</sub>),

lithium salts of the above brominated flame retardant containing hydroxyl groups, or  
10 combinations thereof.

The electrolyte flame retardant composition may further contain other additives such as to facilitate the formation of a solid electrolyte interphase ("SEI") or film to further improve cycle characteristics.

15 The other additives may be, for example, tris(trimethyl silyl) phosphate, lithium difluoro (oxalato) borate, vinylene carbonate, propane sultone, succinonitrile, LiBF<sub>4</sub>, a silane compound

including a functional group that may form a siloxane bond, such as acryl, amino, epoxy, methoxy, ethoxy, or vinyl, or a silazane compound such as hexamethyldisilazane. The additives may be added alone or as a mixture of two or more thereof.

5 The other additives may be included in an amount of about 0.01 wt % to about 10 wt %, based on a total weight of the organic solvent. For example, the other additives may be included in an amount of about 0.05 wt % to about 10 wt %, or about 0.1 wt % to about 5 wt %, or about 0.5 wt % to about 4 wt %, based on the total weight of the organic solvent. However, the amount of these additives are not particularly limited as long as the use of the other additives does not substantially decrease improvement effects on capacity retention rates obtained from the use of  
10 the electrolyte.

The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention. All percentages in the following examples are by weight unless otherwise noted.

### EXAMPLES

15 The Examples were prepared in a glove box by dissolving the 2 weight percent of the flame retardant (FR) in a solution of 1.2 M LiPF<sub>6</sub> in ethylene carbonate / ethylmethyl carbonate (EC/EMC 3/7 wt/wt). Solutions were shaken for 24 hours to solubilize the flame retardants. The flame retardants studied were tetrabromobisphenol A (TBBPA), tribromoneopentyl alcohol (TBNPA), 2,3-dibromo-2-propen-1-ol (DBAA), dibromoethyldibromocyclohexane (BCL-462)  
20 and tetrabromobisphenol A-bis(2,3-dibromopropyl ether) (HP-800).

The test procedure was modeled on a procedure published by D. Peramunage, J.M. Ziegelbaur, G.L. Holleck, *Proc. Electrochem. Soc.*, **2001-21**, 306 (2001), where they used a UL-94 Horizontal Burn (HB) test apparatus. A 1/4 inch wire mesh was placed to hold the sample in the horizontal position. The samples were thin cylindrical fiber glass wicks, 5 inch X 1/8 inch  
25 (Pepperell Braiding Company) which were dried at 120° C for 24 hours then transferred to a desiccator. The 1.2 M LiPF<sub>6</sub> solution (0.75 g) was added drop wise onto the wick to cover the whole length. The wick was allowed to equilibrate for 5 minutes before being transferred for flammability testing. The sample was ignited by holding the flame in contact with the end of the

wick for 10 seconds. Time was recorded from the ignition until the flame reached the end of the wick. The burn times were an average of 3 samples.

| Example              | Description                             | Burn time |
|----------------------|-----------------------------------------|-----------|
| 1<br>(Control-No FR) | 1.2 M LiPF <sub>6</sub> in EC/EMC (3/7) | 125       |
| 2<br>(Comparative)   | 2% TBBPA                                | 133       |
| 3                    | 2% TBNPA                                | 138       |
| 4                    | 2% DBAA                                 | 143       |
| 5                    | 2% BCL-462                              | 139       |
| 6                    | 2% HP-800                               | 143       |

5 Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another component, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

The invention described and claimed herein is not to be limited in scope by the specific examples and embodiments herein disclosed, since these examples and embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be

within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

CLAIMS

1. An electrolyte flame-retardant composition comprising: a) an organic solvent; b) a lithium salt; and c) a brominated flame retardant selected from the group consisting of: , tribromoneopentyl alcohol, dibromoneopentyl glycol, 2,4,6-(tris(2,4,6-tribromophenoxy)-1,3,5-  
5 triazine, tetrabromobiphenol, tetrabromobiphenol carbonate, tetrabromobiphenol epoxy, tetrabromobisphenol F, tetrabromobisphenol F carbonate, tetrabromobisphenol F epoxy, tetrabromobisphenol S, tetrabromobisphenol S carbonate, tetrabromobisphenol S epoxy, (tetrabromobiphenol-bis(2,3-dibromopropyl ether)), (tetrabromobiphenol-bis(2,3-dibromo-2-methylpropyl ether)), (tetrabromobisphenol F-bis(2,3-dibromopropyl ether)),  
10 (tetrabromobisphenol F-bis(2,3-dibromo-2-methylpropyl ether)), (tetrabromobisphenol S-bis(2,3-dibromopropyl ether)), (tetrabromobisphenol S-bis(2,3-dibromo-2-methylpropyl ether)), tribromophenol, dibromoethyldibromocyclohexane, tetrabromocyclooctane, bromopropanol, 2,3-dibromo-2-propen-1-ol, 2,3-dibromo-2-buten-1,4-diol, pentabromobenzyl methacrylate, 2,2',6,6'-tetrabromobisphenol A diglycidyl ether, tribromoethylene, 1,3-dibromo-2,2-dimethylpropane,  
15 2,2-bis(bromomethyl)-1,3-dibromopropane, lithium salts of the brominated flame retardant containing hydroxyl groups, and combinations thereof.
2. The composition of claim 1, wherein the lithium salt is  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ ,  $\text{LiClO}_4$ ,  $\text{LiAlO}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiAlF}_4$ ,  $\text{LiBPh}_4$ ,  $\text{LiB}_{10}\text{Cl}_{10}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ ,  $\text{C}_4\text{F}_3\text{SO}_3\text{Li}$ ,  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ ,  $\text{LiN}(\text{C}_x\text{F}_{2x+1}\text{SO}_2)(\text{C}_x\text{F}_{2y+1}\text{SO}_2)$ , wherein x and  
20 y are whole positive numbers,  $\text{CF}_3\text{CO}_2\text{Li}$ ,  $\text{LiCl}$ ,  $\text{LiI}$ , lithium bis(oxalate) borate (LIBOB), a  $\text{C}_1$  to  $\text{C}_6$  aliphatic lithium carbonate, phenyl lithium borate, lithium imide, or combinations thereof.
3. The composition of claim 1, wherein the organic solvent salt is a carbonate-based solvent, an ester-based solvent, an ether-based solvent, a ketone-based solvent, an alcohol-based or combinations thereof.
4. The composition of claim 1, wherein the organic solvent is diethyl carbonate, dimethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, methyl ethyl carbonate, ethylene carbonate, propylene carbonate, butylene carbonate, vinyl ethylene carbonate or combinations thereof.

5. The composition of claim 1, wherein the amount of brominated flame retardant is about 0.001 wt % to about 10 wt %, based on a total weight of the organic solvent.
6. The composition of claim 5, wherein the amount of lithium salt is at a concentration of about 0.1 molar to about 2.5 molar.
- 5 7. A lithium battery comprising a positive electrode, a negative electrode, a separator, and an electrolyte composition, wherein said electrolyte composition comprises the electrolyte flame-retardant composition of claim 1.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/035740

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>INV. H01M10/0567 H01M10/0525 H01M10/42<br>ADD. H01M10/0568 H01M10/0569                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                      |                                                                      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                      |                                                                      |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>H01M<br><br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br><br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>EPO-Internal, WPI Data, INSPEC, COMPENDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                      |                                                                      |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                      |                                                                      |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Citation of document, with indication, where appropriate, of the relevant passages                                   | Relevant to claim No.                                                |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | CN 103 050 730 A (DONGGUAN XFH BATTERY MATERIAL CO., LTD.)<br>17 April 2013 (2013-04-17)<br>abstract<br>examples 1-7 | 1-7                                                                  |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | JP 2013 251211 A (HITACHI LTD.)<br>12 December 2013 (2013-12-12)<br>abstract<br><br>-----<br>-/-                     | 1-7                                                                  |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                      |                                                                      |
| <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> |                                                                                                                      |                                                                      |
| Date of the actual completion of the international search<br><br>2 August 2017                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                      | Date of mailing of the international search report<br><br>16/08/2017 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                      | Authorized officer<br><br>Masson, Jean-Pierre                        |

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/035740

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                                            |                       |
|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                         | Relevant to claim No. |
| A                                                    | <p>US 2006/292450 A1 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.)<br/>28 December 2006 (2006-12-28)<br/>paragraph [0014] - paragraph [0034]<br/>paragraph [0040] - paragraph [0042]<br/>paragraph [0045] - paragraph [0064]<br/>paragraph [0071] - paragraph [0074]<br/>examples 27-29; table 3A<br/>examples 96-98; table 3D<br/>examples 99-102; table 3E<br/>claims 1, 2</p> <p>-----</p> | 1-7                   |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/035740

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|---------------------|
| CN 103050730                              | A  | 17-04-2013          | NONE                       |                     |
| -----                                     |    |                     |                            |                     |
| JP 2013251211                             | A  | 12-12-2013          | NONE                       |                     |
| -----                                     |    |                     |                            |                     |
| US 2006292450                             | A1 | 28-12-2006          | CN 1700502 A               | 23-11-2005          |
|                                           |    |                     | KR 20060050083 A           | 19-05-2006          |
|                                           |    |                     | US 2006292450 A1           | 28-12-2006          |
| -----                                     |    |                     |                            |                     |