(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 106848381 A
(43)申请公布日 2017.06.13

(21)申请号 201710029575.X

(22)申请日 2017.01.16

(71)申请人 广州天赐高新材料股份有限公司
地址 510760 广东省广州市黄埔区云埔工业区东诚片康达路8号

(72)发明人 洪坤光 周邵云 余乐

(74)专利代理机构 广州市华学知识产权代理有限公司 44245
代理人 罗啸秋 裘晖

(51)Int.Cl.
*H01M 10/0525*(2010.01)
*H01M 10/056*(2010.01)
*H01M 10/0569*(2010.01)
*H01M 10/0567*(2010.01)

权利要求书1页 说明书9页

(54)发明名称

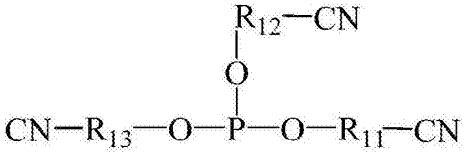
一种电解液及含有该电解液的锂二次电池

(57)摘要

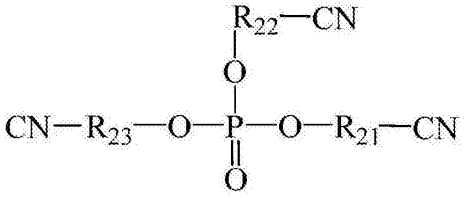
本发明属于锂二次电池领域，公开了一种电解液及含有该电解液的锂二次电池。所述电解液包括电解质、有机溶剂、添加剂和功能化合物，所述功能化合物为三氰基亚磷酸酯化合物和三氰基磷酸酯化合物中的至少一种。本发明的电解液中含有的三氰基亚磷酸酯化合物或三氰基磷酸酯化合物，可以在正负极表面成膜，且能与金属离子络合，防止正极金属离子脱出溶到电解液中和防止其沉积在负极，从而达到稳定正极结构和改善负极SEI膜的作用，提高锂二次电池循环性能和高温性能。同时本发明的功能化合物可降低低温环境下的成膜阻抗，改善低温充电的析锂问题。

CN 106848381 A

1.一种电解液，其特征在于：所述电解液包括电解质、有机溶剂、添加剂和功能化合物，所述功能化合物为三氰基亚磷酸酯化合物和三氰基磷酸酯化合物中的至少一种，所述三氰基亚磷酸酯化合物和三氰基磷酸酯化合物分别具有如下式(I)和式(II)所示的结构式：



式（I），



式（II）；

式中$R_{11}$、$R_{12}$、$R_{13}$、$R_{21}$、$R_{22}$、$R_{23}$各自独立地选自C1～C5的亚烷基或氟代亚烷基。

2.根据权利要求1所述的一种电解液，其特征在于：所述功能化合物在电解液中的质量百分含量为0.05%～10%。

3.根据权利要求2所述的一种电解液，其特征在于：所述功能化合物在电解液中的质量百分含量为0.2%～5%。

4.根据权利要求1所述的一种电解液，其特征在于：所述电解质为$LiPF_6$、$LiBF_4$、$LiSO_3CF_3$、LiBOB、LiDFOB、LiTFSI、LiFSI、$LiPO_2F_2$中的至少一种。

5.根据权利要求1所述的一种电解液，其特征在于：所述有机溶剂包括EC、PC、DMC、DEC、EMC、GBL、MA、EA、PA、BA、MP、EP、PP、BP、MB、EB、PB中的至少两种。

6.根据权利要求5所述的一种电解液，其特征在于：所述有机溶剂为EC、PC、EMC、DEC、PA、MP、EP、PP、EB中的至少两种。

7.根据权利要求1所述的一种电解液，其特征在于：所述添加剂为FEC、VC、VEC、PS、BS、DTD、MMDS、PES、硫酸丙烯酯、亚硫酸乙烯酯、SN、ADN、PN、HTCN、DENE、丁二酸酐、马来酸酐、2-甲基马来酸酐、2,3-二甲基马来酸酐、衣康酸酐中的至少一种。

8.一种锂二次电池，包括含有正极活性材料的正极片、含有负极活性材料的负极片、隔离膜和电解液；正极片包括嵌入或者脱嵌锂离子的正极活性材料、导电剂、集流体及将所述正极活性材料、导电剂、集流体结合的粘结剂；负极片包括可嵌入或者脱嵌锂离子的负极活性材料、导电剂、集流体及将所述负极活性材料、导电剂、集流体结合的粘结剂，其特征在于：所述电解液为权利要求1～7任一项所述的电解液。



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 2 of 23

# 一种电解液及含有该电解液的锂二次电池

## 技术领域

[0001] 本发明属于锂二次电池领域，具体涉及一种电解液及含有该电解液的锂二次电池。

## 背景技术

[0002] 锂二次电池具有工作电压高、比能量密度大、循环寿命长、自放电率低、无记忆效应、对环境污染小等优点，已经广泛应用于消费类电子、储能及动力产品。近年来，随着便携式电子产品向轻便化、高性能发展，这对锂二次电池的能量密度提出更高要求。应对电池更高能量密度的不断追求，业内目前普遍采用的策略是提高正负极的压实和提高电池的截止电压。随之而来的是电池性能的劣化，特别是在高压高温下，电池极片表面形成的SEI膜容易被破坏；在低温充电时，由于电池的动力学性能欠佳，低温充放电时容易析锂，电池安全性能受到影响。

[0003] 专利CN201510564696公开了一种含有双氰基化合物NC-R-CN作为锂离子电池电解液添加剂，可以提高电池的高温存储性能以及循环性能。类似的，专利CN201510964662公开了一种同时含有不饱和碳碳键和氰基的化合物作为锂离子电池电解液添加剂，能够在电极表面发生聚合反应形成含有多个氰基的化合物，该化合物能够与正极材料表面的金属离子络合，从而抑制电解液在电极表面发生分解，提高电池的高温储存及循环性能。但本领域的科研人员发现，含不饱和碳碳双键或三键的化合物成膜阻抗会增大，低温充电时更易析锂，降低电池安全性能。

[0004] 因此，开发一种既能改善高温存储及循环性能，同时又能改善低温充电性能的锂二次电池电解液意义重大。

## 发明内容

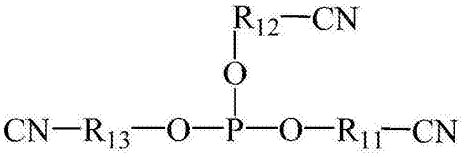
[0005] 本发明的目的在于解决上述技术问题，提供一种既能改善高温存储及循环性能，同时又能改善低温充电性能的电解液及含有该电解液的锂二次电池。

[0006] 本发明目的通过以下技术方案实现：

[0007] 一种电解液，包括电解质、有机溶剂、添加剂和功能化合物，所述功能化合物为三氰基亚磷酸酯化合物和三氰基磷酸酯化合物中的至少一种，所述三氰基亚磷酸酯化合物和三氰基磷酸酯化合物分别具有如下式(I)和式(II)所示的结构式：

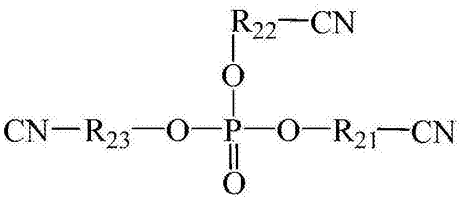


Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 3 of 23



式（I），

[0008]



式（II）；

[0009] 式中$R_{11}$、$R_{12}$、$R_{13}$、$R_{21}$、$R_{22}$、$R_{23}$各自独立地选自C1～C5的亚烷基或氟代亚烷基。

[0010] 所述功能化合物在电解液中的质量百分含量优选为0.05％～10％，当低于0.05％时，不能很好的保护正负极，从而难以充分提高电池的高温储存性能及循环性能，而超过10％时，由于其增加电解液的粘度，导致电池性能恶化。更优选地，其在电解液中的质量百分含量为0.2％～5％。

[0011] 所述电解质优选为六氟磷酸锂（$LiPF_6$）、四氟硼酸锂（$LiBF_4$）、三氟甲基磺酸锂（$LiSO_3CF_3$）、双乙二酸硼酸锂（LiBOB）、二氟草酸硼酸锂（LiDFOB）、双三氟甲烷磺酰亚胺锂（LiTFSI）、双氟磺酰亚胺锂（LiFSI）、二氟磷酸锂

[0012] （$LiPO_2F_2$）的至少一种。

[0013] 所述有机溶剂包括碳酸乙烯酯（EC）、碳酸丙烯酯（PC）、碳酸二甲酯（DMC）、碳酸二乙酯（DEC）、碳酸甲乙酯（EMC）、γ-丁内酯（GBL）、乙酸甲酯（MA）、乙酸乙酯（EA）、乙酸丙酯（PA）、乙酸丁酯（BA）、丙酸甲酯（MP）、丙酸乙酯（EP）、丙酸丙酯（PP）、丙酸丁酯（BP）、丁酸甲酯（MB）、丁酸乙酯（EB）、丁酸丙酯（PB）中的至少两种。

[0014] 优选的，所述有机溶剂为EC、PC、EMC、DEC、PA、MP、EP、PP、EB中的至少两种。

[0015] 所述添加剂为本领域常用的添加剂，作为举例，所述添加剂为氟代碳酸乙烯酯（FEC）、碳酸亚乙烯酯（VC）、碳酸乙烯亚乙酯（VEC）、1,3-丙磺酸内酯（PS）、1,4-丁磺酸内酯（BS）、硫酸乙烯酯（DTD）、甲烷二磺酸亚甲酯（MMDS）、丙烯磺酸内酯（PES）、硫酸丙烯酯、亚硫酸乙烯酯、丁二腈（SN）、己二腈（ADN）、庚二腈（PN）、1,3,6-己烷三腈（HTCN）、乙二醇双（丙腈）醚（DENE）、丁二酸酐、马来酸酐、2-甲基马来酸酐、2,3-二甲基马来酸酐、衣康酸酐中的至少一种。

[0016] 本发明还涉及一种含有上述电解液的锂二次电池，包括含有正极活性材料的正极片、含有负极活性材料的负极片、隔离膜和上述电解液；正极片包括嵌入或者脱嵌锂离子的正极活性材料、导电剂、集流体及将所述正极活性材料、导电剂、集流体结合的粘结剂；负极片包括可嵌入或者脱嵌锂离子的负极活性材料、导电剂、集流体及将所述负极活性材料、导电剂、集流体结合的粘结剂。

[0017] 本发明的电解液具有如下优点及有益效果：

[0018] 本发明的电解液中含有的三氰基亚磷酸酯化合物或三氰基磷酸酯化合物，可以在正负极表面成膜，且能与金属离子络合，防止正极金属离子脱出溶到电解液中和防止其沉积在负极，从而达到稳定正极结构和改善负极SEI膜的作用，提高锂二次电池循环性能和高



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 4 of 23

温性能。同时本发明的功能化合物可降低低温环境下的成膜阻抗，改善低温充电的析锂问题，从而显著提高电池的安全性能。

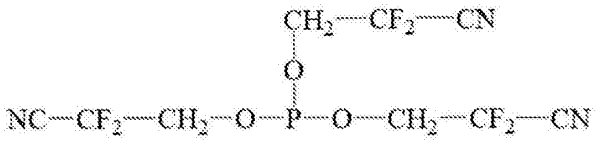
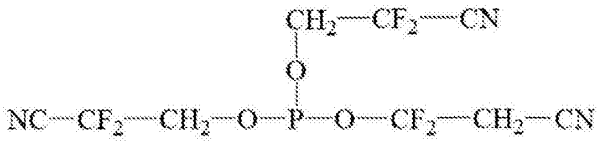
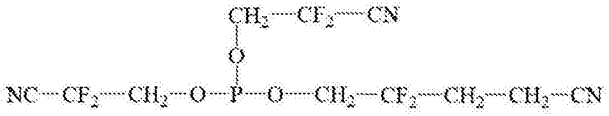
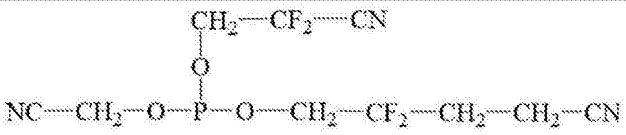
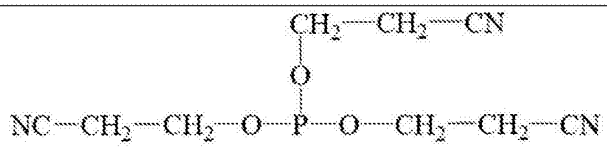
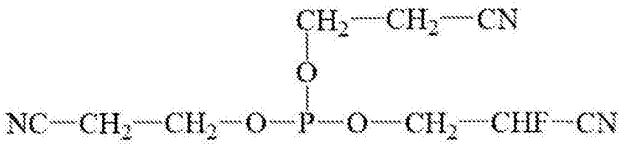
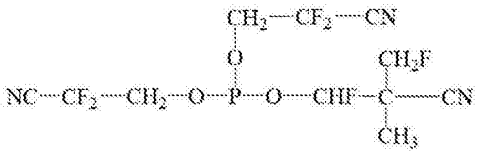
## 具体实施方式

[0019] 下面结合实施例对本发明作进一步详细的描述，但本发明的实施方式不限于此。

[0020] 本发明实施例所用到的三氰基亚磷酸酯化合物和三氰基磷酸酯化合物的结构分别如表1和表2所示。

[0021] 表1三氰基亚磷酸酯化合物

[0022]

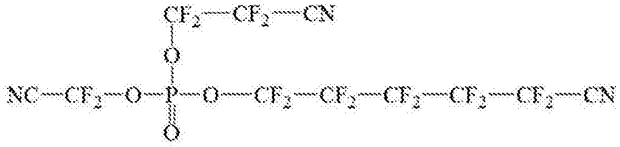
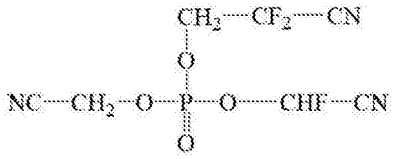
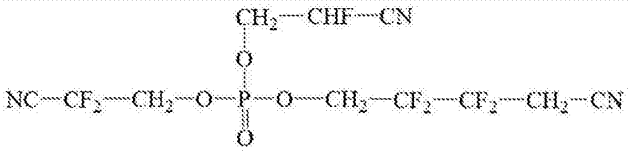
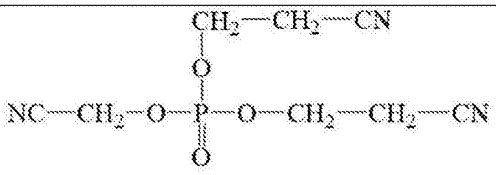
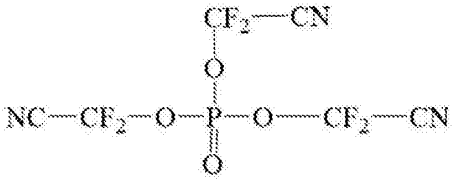
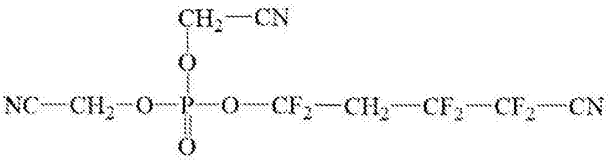
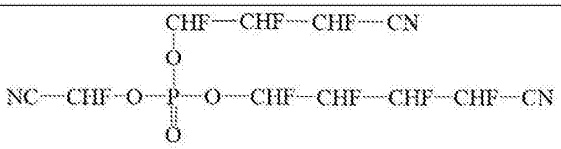
| | 结构式 |
|---|---|
| 化合物$I_1$ |  |
| 化合物 $I_2$ |  |
| 化合物 $I_3$ |  |
| 化合物 $I_4$ |  |
| 化合物 $I_5$ |  |
| 化合物 $I_6$ |  |
| 化合物 $I_7$ |  |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 5 of 23

[0023] 表2三氰基磷酸酯化合物

[0024]

| | 结构式 |
|---|---|
| 化合物$II_1$ |  |
| 化合物 $II_2$ |  |
| 化合物 $II_3$ |  |
| 化合物 $II_4$ |  |
| 化合物 $II_5$ |  |
| 化合物 $II_6$ |  |
| 化合物 $II_7$ |  |

[0025] 本发明实施例中锂二次电池的制备及性能测试步骤如下：

[0026] (1)电解液的制备：在氩气氛围的手套箱中，将有机溶剂按一定质量比混合，再加入添加剂、三氰基亚磷酸酯化合物或三氰基磷酸酯化合物、电解质充分搅拌均匀，即得到本发明所述的电解液。



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 6 of 23

[0027] (2)正极极片的制备:将一定质量比的聚偏氟乙烯(PVDF)溶解于1-甲基-2-吡咯烷酮(NMP)溶液中,再将一定质量比的正极活性材料和导电剂加入上述溶液并混合均匀,将混制的浆料涂布在铝箔的两面后,烘干、辊压后得到正极极片。

[0028] (3)负极极片的制备:将质量比的SBR粘结剂和CMC增稠剂溶于水溶液中,再将一定质量比的负极材料和导电剂加入上述溶液并混合均匀,将混制的浆料涂布在铜箔的两面后,烘干、辊压后得到负极极片。

[0029] (4)锂二次电池的制备:将上述制备的正极极片、负极极片和隔离膜制成电芯,注入步骤(1)所得电解液,经化成等工艺后制成锂二次电池。

[0030] (5)电池性能测试

[0031] 高温循环测试:在45℃恒温箱中以0.5/0.5C的倍率对电池进行充放电循环测试。高温储存性能测试:先将电池在常温状态下以0.5/0.5C的倍率对电池进行充放电一次,再以0.5C将电池充满电后进行高温存储,存储一定时间后热态测试电池的厚度,待电池完全冷却后以0.5C进行充放电测试计算容量保持率和容量恢复率。低温充电测试:先将电池在常温状态下以0.5C放电,再在高低温箱中低温0℃搁置4小时后以0.3C将电池充满电,然后在氩气氛围的手套箱中拆解电池观察负极表面是否析锂。

[0032] 本发明实施例1～25及对比例1～6的电解液组成如表3所示。

[0033] 表3实施例和对比例的电解液组分

[0034]

| | 有机溶剂 | 添加剂 | 功能化合物 | 电解质 |
|---|---|---|---|---|
| 实施例 1 | EC:EMC:DEC:PC=25:25:40:10 | 5%FEC | 3%化合物 $I_1$ | 1.1 M $LiPF_6$ |
| 实施例 2 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_1$ | 1.1 M $LiPF_6$ |
| 实施例 3 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_2$ | 1.1 M $LiPF_6$ |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 7 of 23

[0035]

| | | | | |
|---|---|---|---|---|
| 实施例 4 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_3$ | 1.1 M $LiPF_6$ |
| 实施例 5 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_4$ | 1.1 M $LiPF_6$ |
| 实施例 6 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_5$ | 1.1 M $LiPF_6$ |
| 实施例 7 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_6$ | 1.1 M $LiPF_6$ |
| 实施例 8 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $I_7$ | 1.1 M $LiPF_6$ |
| 实施例 9 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_1$ | 1.1 M $LiPF_6$ |
| 实施例 10 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_2$ | 1.1 M $LiPF_6$ |
| 实施例 11 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_3$ | 1.1 M $LiPF_6$ |
| 实施例 12 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_4$ | 1.1 M $LiPF_6$ |
| 实施例 13 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_5$ | 1.1 M $LiPF_6$ |
| 实施例 14 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_6$ | 1.1 M $LiPF_6$ |
| 实施例 15 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物 $II_7$ | 1.1 M $LiPF_6$ |
| 实施例 16 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.05%化合物 $I_1$ | 1.1 M $LiPF_6$ |
| 实施例 17 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.2%化合物 $I_1$ | 1.1 M $LiPF_6$ |
| 实施例 18 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 5%化合物 $I_1$ | 1.1 M $LiPF_6$ |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 8 of 23

[0036]

| | | | | |
|---|---|---|---|---|
| 实施例19 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 10%化合物$I_1$ | 1.1 M $LiPF_6$ |
| 实施例20 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.4%化合物$I_1$，0.4%化合物$II_2$ | 1.1 M $LiPF_6$ |
| 实施例21 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.4%化合物$I_2$，0.4%化合物$II_5$ | 1.1 M $LiPF_6$ |
| 实施例22 | EC:PA:EP:DEC:PC=25:20:20:25:10 | 3%PS，5%FEC，2%ADN，1%SN，0.5%PES，1%DENE，0.5%衣康酸酐 | 1.0%化合物$II_4$ | 1.0 M $LiPF_6$+0.1 M $LiPO_2F_2$ |
| 实施例23 | EC:MP:EB:DEC:PC=25:20:20:25:10 | 4%PS，6%FEC，1%DENE，1%PN，0.3%VEC，1%DENE，0.5%马来酸酐 | 2.0%化合物$I_7$ | 0.9 M LiFSI |
| 实施例24 | EC:EA:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | 0.8%化合物$I_1$ | 1.1 M $LiPF_6$ |
| 实施例25 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.5%DTD，1%DENE，0.5%HTCN | 1.5%化合物$II_6$ | 1.0 M $LiPF_6$+0.5 M LiTFSI |
| 对比例1 | EC:EMC:DEC:PC=25:25:40:10 | 5%FEC | -- | 1.1 M $LiPF_6$ |
| 对比例2 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.3%VEC，1%DENE | -- | 1.1 M $LiPF_6$ |
| 对比例3 | EC:PA:EP:DEC:PC=25:20:20:25:10 | 3%PS，5%FEC，2%ADN，1%SN，0.5%PES，1%DENE，0.5%衣康酸酐 | -- | 1.0 M $LiPF_6$+0.1 M $LiPO_2F_2$ |
| 对比例4 | EC:MP:EB:DEC:PC=25:20:20:25:10 | 4%PS，6%FEC，1%DENE，1%PN，0.3%VEC，1%DENE，0.5%马来酸酐 | -- | 0.9 M LiFSI |
| 对比例5 | EC:EA:DEC:PC=25 | 3%PS，5%FEC，2%ADN， | -- | 1.1 M |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 9 of 23

[0037]

| | | | | |
|---|---|---|---|---|
| | :25:40:10 | 1%SN，0.3%VEC，1%DENE | | $LiPF_6$ |
| 对比例 6 | EC:PP:DEC:PC=25:25:40:10 | 3%PS，5%FEC，2%ADN，1%SN，0.5%DTD，1%DENE，0.5%HTCN | -- | 1.0 M $LiPF_6$+0.5 M LiTFSI |

[0038] 表中百分含量是指占最终电解液中的质量百分含量，浓度是指在最终电解液中的浓度。

[0039] 实施例1～25和对比例1～6的电解液得到的锂二次电池的性能测试结果如表4所示。

[0040] 表4实施例和对比例的测试结果

[0041]

| | 45℃循环 500 周 | | 60℃满电存储 30 天 | | | 低温 0℃充电 |
|---|---|---|---|---|---|---|
| | 容量保持率/% | 厚度变化率/% | 容量保持率/% | 容量恢复率/% | 厚度变化率/% | |
| 实施例 1 | 86.9 | 4.9 | 78.2 | 87.5 | 8.6 | 未析锂 |
| 实施例 2 | 85.6 | 4.5 | 77.2 | 86.3 | 9.2 | 未析锂 |
| 实施例 3 | 84.5 | 4.1 | 78.1 | 85.2 | 9.5 | 未析锂 |
| 实施例 4 | 85.8 | 4.6 | 77.1 | 85.8 | 8.3 | 未析锂 |
| 实施例 5 | 83.1 | 4.9 | 76.5 | 86.9 | 7.6 | 未析锂 |
| 实施例 6 | 82.9 | 5.3 | 78.2 | 87.1 | 9.3 | 未析锂 |
| 实施例 7 | 83.5 | 4.8 | 77.5 | 87.8 | 7.1 | 未析锂 |
| 实施例 8 | 83.3 | 4.2 | 77.3 | 87.2 | 8.2 | 未析锂 |
| 实施例 9 | 86.2 | 3.8 | 76.5 | 85.3 | 9.8 | 未析锂 |
| 实施例 10 | 83.4 | 4.6 | 78.5 | 88.7 | 6.4 | 未析锂 |
| 实施例 11 | 82.1 | 4.6 | 76.1 | 85.8 | 9.2 | 未析锂 |
| 实施例 12 | 84.6 | 4.1 | 76.6 | 86.5 | 8.2 | 未析锂 |
| 实施例 13 | 84.8 | 4.5 | 78.1 | 89.4 | 6.1 | 未析锂 |
| 实施例 14 | 85.5 | 4.0 | 76.3 | 86.3 | 9.1 | 未析锂 |
| 实施例 15 | 85.2 | 4.3 | 76.1 | 86.8 | 9.5 | 未析锂 |
| 实施例 16 | 80.2 | 6.2 | 72.1 | 80.2 | 12.6 | 未析锂 |
| 实施例 17 | 83.9 | 5.3 | 75.3 | 84.5 | 10.5 | 未析锂 |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 10 of 23

[0042]

| | | | | | | |
|---|---|---|---|---|---|---|
| 实施例 18 | 85.6 | 4.1 | 77.8 | 87.9 | 7.4 | 未析锂 |
| 实施例 19 | 85.3 | 4.9 | 75.5 | 85.2 | 8.2 | 未析锂 |
| 实施例 20 | 86.2 | 4.2 | 78.8 | 89.6 | 6.3 | 未析锂 |
| 实施例 21 | 89.3 | 4.1 | 77.9 | 88.2 | 8.2 | 未析锂 |
| 实施例 22 | 86.6 | 3.6 | 78.3 | 88.5 | 8.9 | 未析锂 |
| 实施例 23 | 88.1 | 3.8 | 77.5 | 89.2 | 6.5 | 未析锂 |
| 实施例 24 | 78.9 | 9.2 | 69.1 | 75.2 | 13.5 | 未析锂 |
| 实施例 25 | 87.2 | 3.5 | 75.1 | 82.6 | 8.2 | 未析锂 |
| 对比例 1 | 75.6 | 7.6 | 65.2 | 75.2 | 22.3 | 析锂 |
| 对比例 2 | 73.1 | 8.5 | 67.1 | 77.4 | 19.3 | 析锂 |
| 对比例 3 | 74.3 | 7.3 | 67.5 | 77.6 | 19.5 | 析锂 |
| 对比例 4 | 75.3 | 7.2 | 65.3 | 76.2 | 20.2 | 析锂 |
| 对比例 5 | 61.1 | 13.9 | 43.5 | 45.6 | 65.4 | 轻微析锂 |
| 对比例 6 | 74.1 | 7.1 | 67.9 | 77.3 | 17.2 | 轻微析锂 |

[0043] 通过实施例1～25与对比例1～6进行对比，发现加入三氰基亚磷酸酯化合物或三氰基磷酸酯化合物可以有效改善电池的循环性能，能明显提高电池高温存储后的容量保持率，抑制厚度膨胀，而且对低温充电析锂问题也有改善。

[0044] 上述实施例为本发明较佳的实施方式，但本发明的实施方式并不受上述实施例的限制，其它的任何未背离本发明的精神实质与原理下所作的改变、修饰、替代、组合、简化，均应为等效的置换方式，都包含在本发明的保护范围之内。



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 11 of 23

(19) China National Intellectual Property Administration

# (12) Invention Patent Application

**(10) Application Publication No.:** CN 106848381 A

**(43) Application Publication Date:** Jun 13, 2017

**(21) Application No.:** 201710029575.X

**(22) Application Date:** Jan 16, 2017

**(71) Applicant:** Guangzhou Tinci Materials Technology Co., Ltd.

**Address:** 8 Kangda Road, Dongcheng Area, Yunpu Industrial Zone, Huangpu District, Guangzhou, Guangdong 510760

**(72) Inventors:** HONG Kunguang ZHOU Shaoyun YU Le

**(74) Patent Agency:** Guangzhou Huaxue Intellectual Property Agency Co., Ltd. 44245

**Agents:** LUO Xiaoqiu QIU Hui

**(51) Int. Cl.**

*H01M 10/0525*(2010.01)

*H01M 10/056*(2010.01)

*H01M 10/0569*(2010.01)

*H01M 10/0567*(2010.01)

Claims: 1 page Description: 9 pages

**(54) Name of Invention**

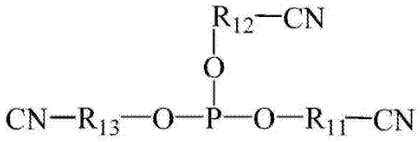
ELECTROLYTE AND LITHIUM SECONDARY BATTERY CONTAINING THE SAME

**(57) Abstract**

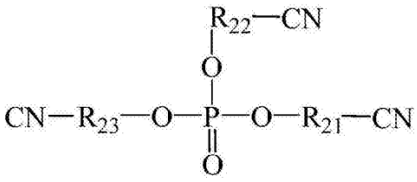
The present invention belongs to the field of lithium secondary batteries and discloses an electrolyte and a lithium secondary battery containing the same. The electrolyte comprises an electrolyte substance, an organic solvent, an additive, and a functional compound, the functional compound being at least one selected from the group consisting of a tricyanophosphite compound and a tricyanophosphate compound. The tricyanophosphite compound or the tricyanophosphate compound contained in the electrolyte of the present invention can form films on the surfaces of the positive and negative electrodes and can complex with metal ions to prevent metal ions at the positive electrode from detaching and dissolving into the electrode and to prevent the metal ions from depositing at the negative electrode, thereby stabilizing the structure of the positive electrode, improving the SEI film at the negative electrode, and improving the cycling performance and high-temperature performance of the lithium secondary battery. At the same time, the functional compound of the present invention can reduce the film impedance in a low-temperature environment and mitigate the issue of lithium precipitation during low-temperature charging.

CN 106848381 A

1. An electrolyte, wherein the electrolyte comprises an electrolyte substance, an organic solvent, an additive, and a functional compound, the functional compound being at least one selected from the group consisting of a tricyanophosphite compound and a tricyanophosphate compound, and the tricyanophosphite compound and the tricyanophosphate compound having, respectively, structural formulas as shown in formula (I) and formula (II) below:



formula (I),



formula (II); and

$R_{11}$, $R_{12}$, $R_{13}$, $R_{21}$, $R_{22}$, and $R_{23}$ in the formulas are each independently selected from the group consisting of C1-C5 alkylene groups and fluoroalkylene groups.

2. The electrolyte of claim 1, wherein the mass percentage of the functional compound in the electrolyte is 0.05%-10%.

3. The electrolyte of claim 2, wherein the mass percentage of the functional compound in the electrolyte is 0.2%-5%.

4. The electrolyte of claim 1, wherein the electrolyte substance is at least one selected from the group consisting of $LiPF_6$, $LiBF_4$, $LiSO_3CF_3$, LiBOB, LiDFOB, LiTFSI, LiFSI, and $LiPO_2F_2$.

5. The electrolyte of claim 1, wherein the organic solvent comprises at least two selected from the group consisting of EC, PC, DMC, DEC, EMC, GBL, MA, EA, PA, BA, MP, EP, PP, BP, MB, EB, and PB.

6. The electrolyte of claim 5, wherein the organic solvent is at least two selected from the group consisting of EC, PC, EMC, DEC, PA, MP, EP, PP, and EB.

7. The electrolyte of claim 1, wherein the additive is at least one selected from the group consisting of FEC, VC, VEC, PS, BS, DTD, MMDS, PES, propylene sulfate, ethylene sulfite, SN, ADN, PN, HTCN, DENE, succinic anhydride, maleic anhydride, 2-methylmaleic anhydride, 2,3-dimethylmaleic anhydride, and itaconic anhydride.

8. A lithium secondary battery, comprising a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, a separator, and an electrolyte; the positive electrode comprising a positive electrode active material for lithium ion intercalation or deintercalation, a conductive agent, a current collector, and a binder that binds the positive electrode active material, the conductive agent, and the current collector; and the negative electrode comprising a negative electrode active material that allows for lithium ion intercalation or deintercalation, a conductive agent, a current collector, and a binder that binds the negative electrode active material, the conductive agent, and the current collector, wherein the electrolyte is the electrolyte of any of claims 1 through 7.



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 13 of 23

# ELECTROLYTE AND LITHIUM SECONDARY BATTERY CONTAINING THE SAME

## TECHNICAL FIELD

[0001] The present invention belongs to the field of lithium secondary batteries and more particularly relates to an electrolyte and a lithium secondary battery containing the same.

## BACKGROUND

[0002] Lithium secondary batteries provide a number of advantages, such as high operating voltage, high energy density, long cycle life, low self-discharge rate, no memory effects, and low pollution to the environment, and have been widely used in consumer electronic products, energy storage products, and power products. In recent years, as portable electronic products trend toward lighter weight and better performance, a higher demand is placed on the energy density of lithium secondary batteries. At present, in response to the continuous pursuit of higher energy density of batteries, a widely used strategy in the industry is to further compact the positive and negative electrodes and improve the cut-off voltage of the batteries. This is accompanied by deterioration of battery performance, and, in particular, it is easy for the SEI film formed on the surface of a battery's electrode to be damaged under a high voltage or a high temperature; during low-temperature charging [*sic*], as the kinetic performance of the battery is less than optimal, it is easy for lithium precipitation to occur during low-temperature charging and discharging, and thus the safety performance of the battery is affected.

[0003] Patent CN201510564696 discloses the use of a dicyano compound NC-R-CN as an additive to the electrolyte of a lithium-ion battery, which is capable of improving the battery's performance for high-temperature storage and cycling. Similarly, Patent CN201510964662 discloses the use of a compound having both an unsaturated carbon-carbon bond and a cyano group as an additive to the electrolyte of a lithium-ion battery; this enables polymerization on an electrode surface to form a compound containing a plurality of cyano groups, and this compound can complex with metal ions on the surface of the positive electrode material, thereby inhibiting the decomposition of the electrolyte at the surface of the electrode and improving the battery's performance for high-temperature storage and cycling. However, researchers in the art have discovered that film formation by a compound containing an unsaturated carbon-carbon double bond or triple bond increases the impedance, which causes lithium precipitation to occur more easily when the battery is charged at a low temperature and thereby lowers the battery's safety performance.

[0004] Therefore, it is of significant importance to develop a lithium secondary battery electrolyte for better high-temperature storage performance, cycling performance, and low-temperature charging performance.

## SUMMARY

[0005] The purpose of the present invention is to address the aforementioned technical issue, i.e., to provide an electrolyte and a lithium secondary battery containing the same for better high-temperature storage performance, cycling performance, and low-temperature charging performance.

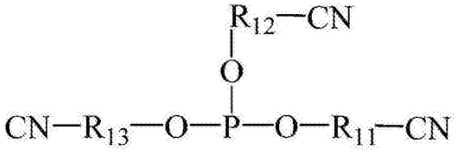
[0006] The purpose of the present invention is achieved through the following technical solution:

[0007] an electrolyte comprising an electrolyte substance, an organic solvent, an additive, and a



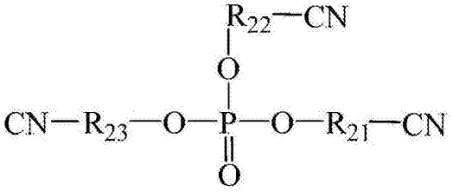
Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 14 of 23

functional compound, the functional compound being at least one selected from the group consisting of a tricyanophosphite compound and a tricyanophosphate compound, and the tricyanophosphite compound and the tricyanophosphate compound having, respectively, structural formulas as shown in formula (I) and formula (II) below:



formula (I),

[0008]



formula (II); and

[0009] $R_{11}$, $R_{12}$, $R_{13}$, $R_{21}$, $R_{22}$, and $R_{23}$ in the formulas are each independently selected from the group consisting of C1-C5 alkylene groups and fluoroalkylene groups.

[0010] Preferably, the mass percentage of the functional compound in the electrolyte is 0.05%-10%; when the percentage is less than 0.05%, the positive and negative electrodes are not well protected so it is difficult to adequately improve the battery's high-temperature storage performance and cycling performance; when the percentage is greater than 10%, increased viscosity of the electrolyte leads to deterioration of the battery's performance. More preferably, the mass percentage of the functional compound in the electrolyte is 0.2%-5%.

[0011] Preferably, the electrolyte substance is at least one selected from the group consisting of lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium trifluoromethanesulfonate ($LiSO_3CF_3$), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), lithium bis(trifluoromethylsulphonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium difluorophosphate

[0012] ($LiPO_2F_2$).

[0013] The organic solvent comprises at least two selected from the group consisting of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), γ-butyrolactone (GBL), methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), methyl propionate (MP), ethyl propionate (EP), propyl propionate (PP), butyl propionate (BP), methyl butyrate (MB), ethyl butyrate (EB), and propyl butyrate (PB).

[0014] Preferably, the organic solvent is at least two selected from the group consisting of EC, PC, EMC, DEC, PA, MP, EP, PP, and EB.

[0015] The additive is a common additive used in the art; for example, the additive is at least one selected from the group consisting of fluoroethylene carbonate (FEC), vinylene carbonate (VC), vinyl ethylene carbonate (VEC), 1,3-propane sultone (PS), 1,4-butane sultone (BS), ethylene sulfate (DTD), methylene methanedisulfonate (MMDS), prop-1-ene-1,3-sultone (PES), propylene sulfate, ethylene sulfite, succinonitrile (SN), adiponitrile (ADN), pimelonitrile (PN), 1,3,6-hexanetricarbonitrile (HTCN), ethylene glycol bis(propionitrile) ether (DENE), succinic anhydride, maleic anhydride, 2-methylmaleic anhydride, 2,3-dimethylmaleic anhydride, and itaconic anhydride.



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 15 of 23

[0016] The present invention also relates to a lithium secondary battery containing the aforementioned electrolyte, the lithium secondary battery comprising a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, a separator, and the aforementioned electrolyte; the positive electrode comprising a positive electrode active material for lithium ion intercalation or deintercalation, a conductive agent, a current collector, and a binder that binds the positive electrode active material, the conductive agent, and the current collector; and the negative electrode comprising a negative electrode active material that allows for lithium ion intercalation or deintercalation, a conductive agent, a current collector, and a binder that binds the negative electrode active material, the conductive agent, and the current collector.

[0017] The electrolyte of the present invention provides the following advantages and benefits:

[0018] the tricyanophosphite compound or the tricyanophosphate compound contained in the electrolyte of the present invention can form films on the surfaces of the positive and negative electrodes and can complex with metal ions to prevent metal ions at the positive electrode from detaching and dissolving into the electrode and to prevent the metal ions from depositing at the negative electrode, thereby stablizing the structure of the positive electrode, improving the SEI film at the negative electrode, and improving the cycling performance and high-temperature performance of the lithium secondary battery. At the same time, the functional compound of the present invention can reduce the film impedance in a low-temperature environment, mitigate the issue of lithium precipitation during low-temperature charging, and thereby significantly improve the safety performance of the battery.

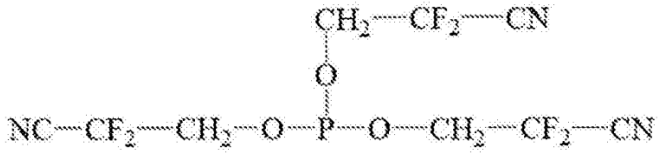
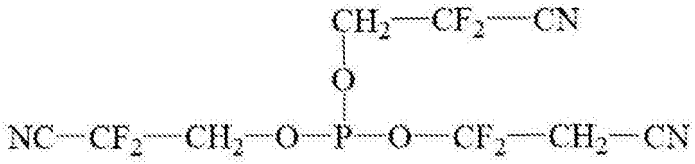
## DETAILED DESCRIPTION

[0019] A more detailed description of the present invention is provided below in conjunction with embodiments; however, the present invention are not limited thereby.

[0020] The structures of the tricyanophosphite compounds and the tricyanophosphate compounds used in embodiments of the present invention are shown in Table 1 and Table 2, respectively.

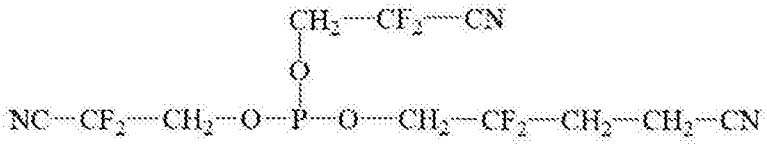
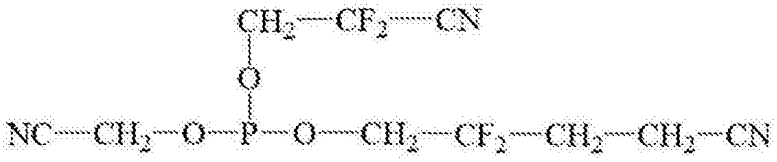
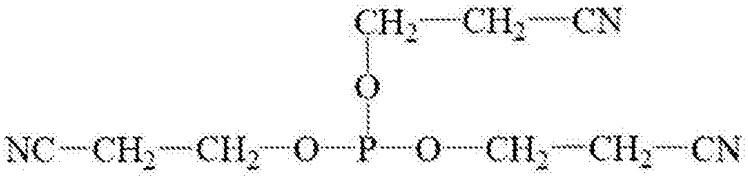
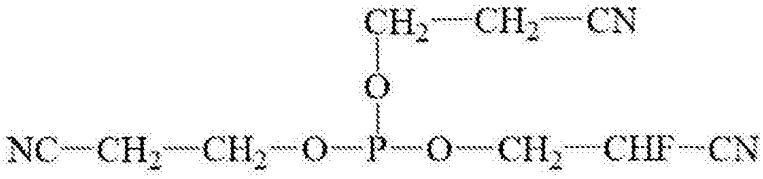
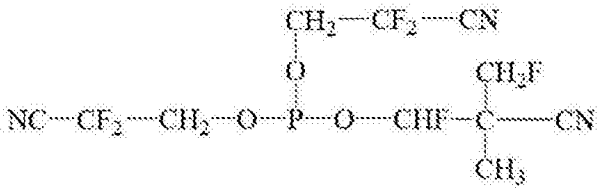
[0021] Table 1 Tricyanophosphite compounds

[0022]

| | Structural formula |
|---|---|
| Compound $I_1$ |  |
| Compound $I_2$ |  |

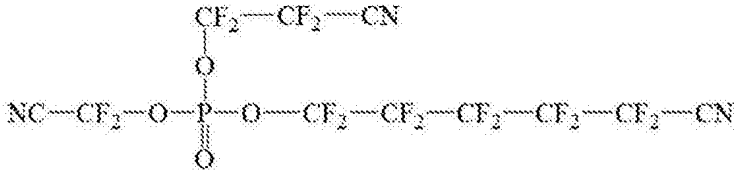
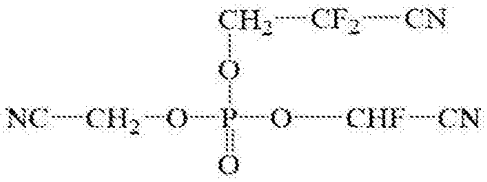


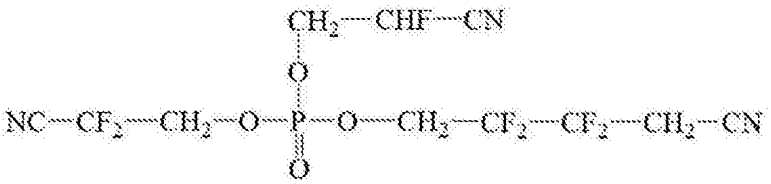
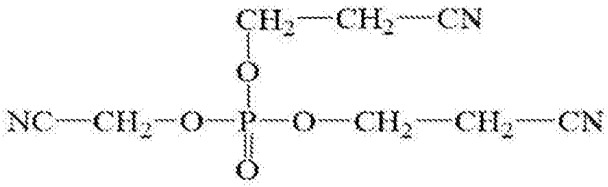
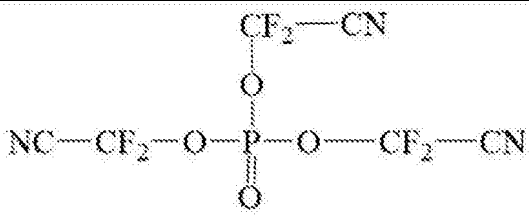
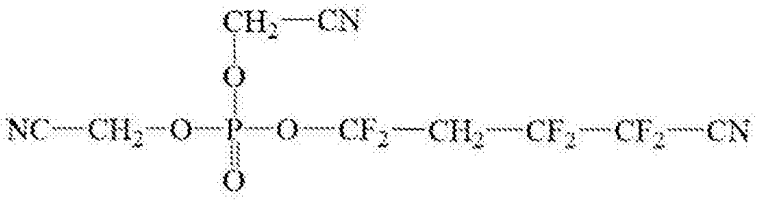
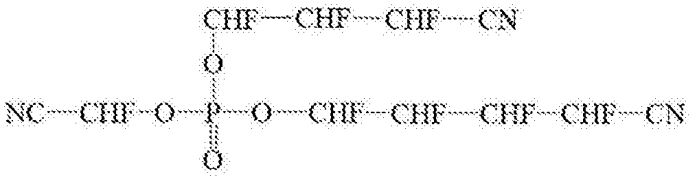
Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 16 of 23

| | |
|---|---|
| Compound $I_3$ |  |
| Compound $I_4$ |  |
| Compound $I_5$ |  |
| Compound $I_6$ |  |
| Compound $I_7$ |  |

[0023] Table 2 Tricyanophosphate compounds

[0024]

| | Structural formula |
|---|---|
| Compound $II_1$ |  |
| Compound $II_2$ |  |

| | |
|---|---|
| Compound $II_3$ |  |
| Compound $II_4$ |  |
| Compound $II_5$ |  |
| Compound $II_6$ |  |
| Compound $II_7$ |  |

[0025] Below are the steps for the manufacturing and performance testing of the lithium secondary battery according to embodiments of the present invention:

[0026] (1) Electrolyte preparation: mixing, in an argon atmosphere glove box, organic solvents according to a mass ratio; and then adding an additive, a tricyanophosphite compound or tricyanophosphate compound, and an electrolyte substance and stirring well to obtain the electrolyte of the present invention.

[0027] (2) Positive electrode preparation: dissolving polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidone (NMP) according to a mass ratio; then adding a positive electrode active material and a conductive agent to the aforementioned solution according to a mass ratio and mixing well; coating two surfaces of an aluminum foil with the mixed slurry; and performing drying and calendaring to obtain a positive electrode.

[0028] (3) Negative electrode preparation: dissolving a SBR binder and a CMC thickener in water according to a mass ratio; then adding a negative electrode material and a conductive agent to the aforementioned solution according to a mass ratio and mixing well; coating two surfaces of a copper foil with the mixed slurry; and performing drying and calendaring it to obtain a negative electrode.

[0029] (4) Lithium secondary battery manufacturing: making the positive electrode, the negative electrode, and the separator prepared above into a cell; injecting the electrolyte obtained in Step (1); and performing formation and other process steps to complete a lithium secondary battery.

[0030] (5) Battery performance testing

[0031] High-temperature cycle test: performing a charge/discharge cycle test on the battery at 0.5/0.5 C rate in a 45 °C temperature chamber. High-temperature storage performance test: performing charging and discharging of the battery once at 0.5/0.5 C rate in room temperature; then storing the battery at a high temperature after fully charging it at 0.5 C rate; performing a hot test on the thickness of the battery after it has been stored for a period of time; and performing a charge/discharge test at 0.5 C rate once the battery has cooled completely to calculate its capacity retention rate and capacity recovery rate. Low-temperature charge test: discharging the battery at 0.5 C rate in room temperature; fully charging the battery at 0.3 C rate after resting it in a high/low temperature chamber at 0 °C for 4 hours; and then disassembling the battery in an argon atmosphere glove box and observing whether lithium precipitation has occurred on the surface of the negative electrode.

[0032] The composition of the electrolyte in Embodiments 1-25 and Comparison Cases 1-6 of the present invention are shown in Table 3.

[0033] Table 3 Electrolyte composition in embodiments and comparison cases

[0034]

| | Organic solvent | Additive | Functional compound | Electrolyte substance |
|---|---|---|---|---|
| Embodiment 1 | EC:EMC:DEC:PC = 25:25:40:10 | 5% FEC | 3% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 2 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 3 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_2$ | 1.1 M $LiPF_6$ |

[0035]

| | | | | |
|---|---|---|---|---|
| Embodiment 4 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_3$ | 1.1 M $LiPF_6$ |
| Embodiment 5 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_4$ | 1.1 M $LiPF_6$ |
| Embodiment 6 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_5$ | 1.1 M $LiPF_6$ |
| Embodiment 7 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_6$ | 1.1 M $LiPF_6$ |
| Embodiment 8 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_7$ | 1.1 M $LiPF_6$ |
| Embodiment 9 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_1$ | 1.1 M $LiPF_6$ |
| Embodiment 10 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_2$ | 1.1 M $LiPF_6$ |



Zhuhai CosMX Battery Co. - EX1015
Zhuhai CosMX Battery Co. v. Ningde Amperex Tech. Ltd.
IPR2025-00431
Page 19 of 23

| | | | | |
|---|---|---|---|---|
| Embodiment 11 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_3$ | 1.1 M $LiPF_6$ |
| Embodiment 12 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_4$ | 1.1 M $LiPF_6$ |
| Embodiment 13 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_5$ | 1.1 M $LiPF_6$ |
| Embodiment 14 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_6$ | 1.1 M $LiPF_6$ |
| Embodiment 15 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $II_7$ | 1.1 M $LiPF_6$ |
| Embodiment 16 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.05% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 17 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.2% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 18 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 5% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 19 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 10% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 20 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.4% Compound $I_1$, 0.4% Compound $II_2$ | 1.1 M $LiPF_6$ |
| Embodiment 21 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.4% Compound $I_2$, 0.4% Compound $II_5$ | 1.1 M $LiPF_6$ |
| Embodiment 22 | EC:PA:EP:DEC:PC = 25:20:20:25:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.5% PES, 1% DENE, 0.5% itaconic anhydride | 1.0% Compound $II_4$ | 1.0 M $LiPF_6$ +0.1 M $LiPO_2F_2$ |
| Embodiment 23 | EC:MP:EB:DEC:PC = 25:20:20:25:10 | 4% PS, 6% FEC, 1% DENE, 1% PN, 0.3% VEC, 1% DENE, 0.5% maleic anhydride | 2.0% Compound $I_7$ | 0.9 M LiFSI |
| Embodiment 24 | EC:EA:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | 0.8% Compound $I_1$ | 1.1 M $LiPF_6$ |
| Embodiment 25 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.5% DTD, 1% DENE, 0.5% HTCN | 1.5% Compound $II_6$ | 1.0 M $LiPF_6$ +0.5 M LiTFSI |
| Comparison Case 1 | EC:EMC:DEC:PC = 25:25:40:10 | 5% FEC | -- | 1.1 M $LiPF_6$ |
| Comparison Case 2 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | -- | 1.1 M $LiPF_6$ |
| Comparison Case 3 | EC:PA:EP:DEC:PC = 25:20:20:25:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.5% PES, 1% DENE, 0.5% itaconic anhydride | -- | 1.0 M $LiPF_6$ +0.1 M $LiPO_2F_2$ |
| Comparison Case 4 | EC:MP:EB:DEC:PC = 25:20:20:25:10 | 4% PS, 6% FEC, 1% DENE, 1% PN, 0.3% VEC, 1% DENE, 0.5% maleic anhydride | -- | 0.9 M LiFSI |
| Comparison Case 5 | EC:EA:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.3% VEC, 1% DENE | -- | 1.1 M $LiPF_6$ |
| Comparison Case 6 | EC:PP:DEC:PC = 25:25:40:10 | 3% PS, 5% FEC, 2% ADN, 1% SN, 0.5% DTD, 1% DENE, 0.5% HTCN | -- | 1.0 M $LiPF_6$ +0.5 M LiTFSI |

[0038] In the table, percentage refers to the mass percentage in the final electrolyte, and concentration

refers to the concentration in the final electrolyte.

[0039] Results from the performance testing of the lithium secondary battery made with the electrolyte according to Embodiments 1-25 and Comparison Cases 1-6 are shown in Table 4.

[0040] Table 4 Testing results for embodiments and comparison cases

[0041]

| | 45 ºC, 500 cycles | | 60 ºC, fully charged, stored for 30 days | | | Low-temperature charge at 0 ºC |
|---|---|---|---|---|---|---|
| | Capacity retention rate /% | Thickness change rate /% | Capacity retention rate /% | Capacity recovery rate /% | Thickness change rate /% | |
| Embodiment 1 | 86.9 | 4.9 | 78.2 | 87.5 | 8.6 | No lithium precipitation |
| Embodiment 2 | 85.6 | 4.5 | 77.2 | 86.3 | 9.2 | No lithium precipitation |
| Embodiment 3 | 84.5 | 4.1 | 78.1 | 85.2 | 9.5 | No lithium precipitation |
| Embodiment 4 | 85.8 | 4.6 | 77.1 | 85.8 | 8.3 | No lithium precipitation |
| Embodiment 5 | 83.1 | 4.9 | 76.5 | 86.9 | 7.6 | No lithium precipitation |
| Embodiment 6 | 82.9 | 5.3 | 78.2 | 87.1 | 9.3 | No lithium precipitation |
| Embodiment 7 | 83.5 | 4.8 | 77.5 | 87.8 | 7.1 | No lithium precipitation |
| Embodiment 8 | 83.3 | 4.2 | 77.3 | 87.2 | 8.2 | No lithium precipitation |
| Embodiment 9 | 86.2 | 3.8 | 76.5 | 85.3 | 9.8 | No lithium precipitation |
| Embodiment 10 | 83.4 | 4.6 | 78.5 | 88.7 | 6.4 | No lithium precipitation |
| Embodiment 11 | 82.1 | 4.6 | 76.1 | 85.8 | 9.2 | No lithium precipitation |
| Embodiment 12 | 84.6 | 4.1 | 76.6 | 86.5 | 8.2 | No lithium precipitation |
| Embodiment 13 | 84.8 | 4.5 | 78.1 | 89.4 | 6.1 | No lithium precipitation |
| Embodiment 14 | 85.5 | 4.0 | 76.3 | 86.3 | 9.1 | No lithium precipitation |
| Embodiment 15 | 85.2 | 4.3 | 76.1 | 86.8 | 9.5 | No lithium precipitation |
| Embodiment 16 | 80.2 | 6.2 | 72.1 | 80.2 | 12.6 | No lithium precipitation |
| Embodiment 17 | 83.9 | 5.3 | 75.3 | 84.5 | 10.5 | No lithium precipitation |

[0042]

| | | | | | | |
|---|---|---|---|---|---|---|
| Embodiment 18 | 85.6 | 4.1 | 77.8 | 87.9 | 7.4 | No lithium precipitation |
| Embodiment 19 | 85.3 | 4.9 | 75.5 | 85.2 | 8.2 | No lithium precipitation |

| | | | | | | |
|---|---|---|---|---|---|---|
| Embodiment 20 | 86.2 | 4.2 | 78.8 | 89.6 | 6.3 | No lithium precipitation |
| Embodiment 21 | 89.3 | 4.1 | 77.9 | 88.2 | 8.2 | No lithium precipitation |
| Embodiment 22 | 86.6 | 3.6 | 78.3 | 88.5 | 8.9 | No lithium precipitation |
| Embodiment 23 | 88.1 | 3.8 | 77.5 | 89.2 | 6.5 | No lithium precipitation |
| Embodiment 24 | 78.9 | 9.2 | 69.1 | 75.2 | 13.5 | No lithium precipitation |
| Embodiment 25 | 87.2 | 3.5 | 75.1 | 82.6 | 8.2 | No lithium precipitation |
| Comparison Case 1 | 75.6 | 7.6 | 65.2 | 75.2 | 22.3 | Lithium precipitation |
| Comparison Case 2 | 73.1 | 8.5 | 67.1 | 77.4 | 19.3 | Lithium precipitation |
| Comparison Case 3 | 74.3 | 7.3 | 67.5 | 77.6 | 19.5 | Lithium precipitation |
| Comparison Case 4 | 75.3 | 7.2 | 65.3 | 76.2 | 20.2 | Lithium precipitation |
| Comparison Case 5 | 61.1 | 13.9 | 43.5 | 45.6 | 65.4 | Slight lithium precipitation |
| Comparison Case 6 | 74.1 | 7.1 | 67.9 | 77.3 | 17.2 | Slight lithium precipitation |

[0043] By comparing Embodiments 1-25 and Comparison Cases 1-6, it is found that the addition of a tricyanophosphite compound or a tricyanophosphate compound can effectively improve the battery's cycling performance, significantly increase the battery's capacity retention rate after storage at a high temperature, suppress thickness expansion, and mitigate lithium precipitation during low-temperature charging.

[0044] The example embodiments above are better embodiments of the present invention; however, the present invention is not limited by the aforementioned embodiments, and any other alteration, modification, substitution, combination, and simplification made without deviating from the spirit, essence, and principle of the present invention shall be equivalent replacement and shall fall within the scope of protection of the present invention.

**Acta Chinese Language Services, LLC**
www.actalanguage.com | (202)618-2307 | info@actalanguage.com | Gaithersburg, MD

**CERTIFICATE OF ACCURACY**

I, Evelyn Garland, am competent to translate from Chinese into English and certify that the attached English language document(s) is a true and accurate translation of the original Chinese language document(s) CN106848381A to the best of my abilities.

I further declare that the statement in the preceding paragraph is true, and I understand that false statements and the like are punishable by fine and imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Date: January 17, 2023

American Translators Association
ata
Evelyn Yang Garland
Chinese into English
Certification #491044
Certified Translator
Verify at www.atanet.org/verify

Evelyn Yang Garland

*ATA Certified Translator, English<->Chinese*
*Maryland Court Certified Interpreter, English<->Mandarin Chinese*

President
**Acta Chinese Language Services, LLC**

PO Box 3884
Gaithersburg, MD 20885
egarland@actalanguage.com, (202) 618-2307
www.actalanguage.com

American Translators Association
ata
Evelyn Yang Garland
English into Chinese
Certification #491044
Certified Translator
Verify at www.atanet.org/verify