

## Advances on high-voltage electrolyte of lithium ion batteries

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**Abstract:** To satisfy the increasing discharge capacity demand of next generation electric devices, various high working voltage cathodes have been explored. However, traditional carbonate solvents, such as ethylene carbonate and ethyl methyl carbonate-based electrolytes are prone to oxidative decomposition at high voltage ( $>4.3$  V, vs. Li/Li<sup>+</sup>), which results in the increase of irreversible capacity and the inferior cycling performance of lithium ion batteries. To solve the problem, it is necessary to design high-voltage tolerant electrolyte based on theories and experiments. Specifically, new high-voltage solvents such as sulfone and ionic liquid are determining factors to improve the stability of electrolyte as they could improve the interfacial stability between the high voltage cathode and the electrolyte intrinsically. Another method to solve the problem is the addition of high-voltage additives because a small amount of additives could form an effective solid electrolyte interface layer and decrease the interfacial reaction dynamically. Moreover, additives can solve the problem economically and effectively. In addition, optimizing the physical and chemical properties of conventional electrolyte is a new strategy to exhibit new properties. For example, a novel formula such as superconcentrated electrolyte has wide electrochemical window and superior cycling performance. However, it is well known that high voltage solvents are often characterized by high viscosity, low reductive stability and reductive decomposition products cannot form an effective interfacial layer on the anodes. The addition of additives may have negative impact on other properties of lithium ion batteries such as the initial coulombic efficiency. And the superconcentrated electrolyte is very expensive and high viscosity. Although they have some defects, it is also very significant to study them because they can give a guide to investigate electrolyte with superior performance. Thus, this review summarized the advances and perspectives on the development of high-voltage solvents, additives and superconcentrated electrolyte of lithium ion batteries.

### Key learning points:

- (1) High voltage solvents can stabilize the electrode/electrolyte interface intrinsically.
- (2) A small amount of high voltage additives can improve the battery performance economically.
- (3) Superconcentrated electrolyte is characterized by superb properties like high oxidative and reductive stability, Al-anti corrosion and high rate performance.

**Key words:** lithium ion batteries; high-voltage electrolyte; high-voltage solvent; high-voltage additive; superconcentrated electrolyte strategy

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# 锂离子电池高压电解液研究进展

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**摘要:** 传统碳酸酯类电解液在高压(>4.3 V, vs. Li/Li<sup>+</sup>)下易发生氧化分解反应, 导致锂离子电池不可逆容量增加、循环性能下降。为解决这一问题, 需从理论和实验两方面对电解液溶剂、锂盐、添加剂及其基本组成等进行针对性设计。耐高压溶剂是提升电解液稳定性的关键因素之一, 既经济又有效, 添加高浓锂盐是近年来研究较多的可提升电解液电化学窗口和循环稳定性的新策略。本工作从耐高压溶剂、高压添加剂和高浓锂盐三方面综述了近几年锂离子电池高压电解液的研究进展。

**要点:**

(1) 高压溶剂可从本质上提高电解液与电极材料间的界面稳定性。

(2) 高压添加剂用量少、成本低, 能显著提高电池的高压性能。

(3) 高浓锂盐体系具有优异的耐氧化/还原能力, 可以有效预防铝集流体腐蚀, 提高电池的倍率性能。

**关键词:** 锂离子电池; 高压电解液; 高压溶剂; 高压添加剂; 高浓锂盐

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## 1 前言

近年来由于环境污染、能源危机等问题, 世界各国都在大力发展新能源汽车。锂离子电池因其比容量高、无记忆效应、循环寿命长等优点而成功应用于 3C 电子产品、航空航天及信息技术等领域<sup>[1-3]</sup>, 但现有的锂离子电池体系不能满足电动汽车高能量密度及高安全性的要求。目前提高锂离子电池能量密度的方法主要是使用高容量负极材料和高压正极材料。近年来, 高压正极材料如 LiCoPO<sub>4</sub><sup>[4]</sup>, Li<sub>2</sub>CoPO<sub>4</sub>F<sup>[5]</sup>和 LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub><sup>[6]</sup>及富锂正极材料  $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$  (M=Ni, Co, Mn)<sup>[7]</sup>等的发展日新月异, 但由 1 mol/L 六氟磷酸锂(LiPF<sub>6</sub>)溶解于碳酸乙烯酯(EC)、碳酸二甲酯(DMC)、碳酸甲乙酯(EMC)等碳酸酯溶剂中组成的传统商业电解液在电压大于 4.3 V (vs. Li/Li<sup>+</sup>)时易发生氧化分解反应, 使锂离子电池的不可逆容量增大, 导致电池循环性能变差<sup>[8]</sup>。因此, 研发与高压正极材料匹配的电解液体系尤为重要, 常用的方法有设计新型耐高压溶剂、寻找高压电解液添加剂等<sup>[9]</sup>。

根据前线轨道理论, 分子的最高已占轨道(HOMO)能级对电子束缚较松弛, 具有电子给体的性质, 分子的最低未占轨道(LUMO)能级对电子的亲合力较强, 具有电子受体的性质, HOMO 能级升高易失去电子, LUMO 能级降低易得到电子, 因此 HOMO 能级低意味着溶剂的氧化稳定性强, 即氧化电位高, LUMO 能级高意味着溶剂的还原稳定性强, 即还原电位低。

锂离子电池高压电解液添加剂的作用原理为添加剂氧化分解, 在正极表面形成稳定的固体电解质界面膜(CEI 膜), 保护正极材料并抑制电解液氧化分解<sup>[10-12]</sup>。因此可优选 HOMO 能级高的物质作高压电解液添加剂、HOMO 能级低的物质为锂离子电池高压溶剂, 通过实验验证符合该条件的添加剂氧化分解后能否形成有效的 CEI 膜、符合该条件的高压溶剂能否与负极匹配等。此外, 仅在传统碳酸酯溶剂中改变锂盐浓度, 构建新型的电解液体系如高浓锂盐电解液, 就可展现较强的耐氧化能力、耐还原能力、高热稳定性等许多传统浓度电解液没有的优异性能<sup>[13]</sup>。本工作主要从高压溶剂、高压添加剂及高浓锂盐电解液三方面阐述近年来高压电解液的研究进展和面临的挑战。

## 2 高压电解液溶剂

### 2.1 氟代溶剂

氟原子电负性极强, 吸电子能力强, 因此氟代溶剂的 HOMO 能级和 LUMO 能级均低于传统碳酸酯溶剂, 即氟代溶剂的氧化电位和还原电位均高于传统碳酸酯溶剂<sup>[14]</sup>。因此, 氟代溶剂常用作耐高压溶剂或负极固体电解质界面膜(SEI 膜)成膜添加剂。目前已有部分氟代溶剂实现了商业化, 如氟代碳酸乙烯酯(FEC)<sup>[15,16]</sup>、FEC 及三氟碳酸丙烯酯(TFPC)、四氟丙基碳酸丙烯酯醚(TFP-PC-E)、三氟乙基甲基碳酸酯(F-EMC)、二-三氟乙基碳酸酯(HF-DEC)、三氟乙基碳酸乙酯(TF-DEC)的结构见图 1。

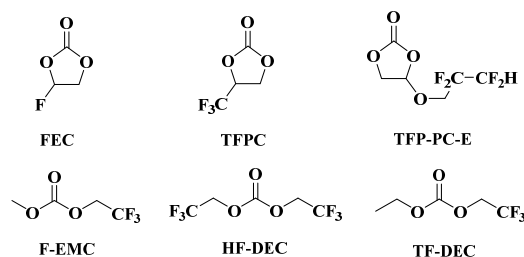


图 1 几种氟代溶剂的结构

Fig.1 The structures of several fluorinated solvents

除 FEC 外, Wang 等<sup>[17]</sup>证明了 3-(1,1,2,2-四氟乙氧基)-1,1,2,2-(四氟丙烷) (F-EPE)在  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  高压正极和石墨负极上的作用. 恒电流充放电测试结果表明,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ /石墨全电池(电压 3.0~4.5 V, 充放电倍率 1 C)在常规电解液  $\text{LiPF}_6\text{-EC:DEC}$ (碳酸二乙酯)(质量比 1:3)中循环 100 次后比容量由最初的 178 mA·h/g 降到 22 mA·h/g, 容量保持率仅有 12%; 与之对比, 加入 20wt% F-EPE 后  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ /石墨全电池在相同条件下循环 100 次后容量保持率大于 74%; 线性伏安测试表明常规电解液在 Pt 电极上 4.7 V 电压下即发生氧化分解, 加入 20wt% F-EPE 的电解液氧化分解电位提高到 5.4 V, 且氧化电流远小于常规电解液, 表明加入 F-EPE 可提高电解液的氧化稳定性. 此外, F-EPE 不仅可提高电解液的耐高压性能, 同时起着负极成膜添加剂的作用. 用扫描电镜观察循环后的石墨负极, 加入 F-EPE 后石墨负极表面形成一层致密的 SEI 膜, 有效阻止了电解液与石墨负极接触, 进一步提高了电池的循环稳定性. Luo 等<sup>[18]</sup>考察了 F-EPE 作为共溶剂对高压正极  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO)的影响, 恒电位极化测试结果表明, 加入 F-EPE 后, LNMO/Li 在 5.0, 5.1, 5.3 和 5.5 V 电压下 2 h 的漏电流均小于常规电解液, 表明加入共溶剂 F-EPE 有助于提高电解液在高压正极 LNMO 上的稳定性. He 等<sup>[19]</sup>采用恒电位极化法分析了系列氟代溶剂及 EC 和 DMC 的电化学稳定性, 结果表明, 环状氟代碳酸酯溶剂的电化学稳定性  $\text{TFPC} > \text{EC} > \text{TFP-PC-E}$ , 线性氟代碳酸酯溶剂的电化学稳定性  $\text{HF-DEC} > \text{F-EMC} > \text{TF-DEC} > \text{DMC}$ , 表明氟代溶剂的氧化稳定性优于传统碳酸酯溶剂.

## 2.2 砜类溶剂

磺酰基的电负性比羰基强, 因而砜类溶剂的 HOMO 能级低于传统碳酸酯溶剂, 具有高于传统碳酸酯溶剂的电化学稳定性<sup>[20]</sup>. 此外, 砜类溶剂与其它高压溶剂相比有两个优点: (1) 磺酰基与锂盐的相互作用强, 利于实现高电导率; (2) 耐燃烧性好, 符合高安全电解液的标准. 因此砜类溶剂近年来广受关注<sup>[21]</sup>.

Shao 等<sup>[21]</sup>用 B3LYP/6-31+G(d,p), HF/6-31+G(d,p), PBE/6-31+G(d,p)和 MP2/6-31+G(d,p)四种方法对乙基甲氧基乙氧基乙基砜(EMEES)、乙基甲基砜(EMS)、乙基甲氧基乙基砜(EMES)和甲氧基乙基甲基砜(MEMS)(结构如图 2 所示)进行理论计算, 结果表明其电化学窗口均大于 5 V. Wu 等<sup>[22]</sup>通过理论计算及电化学测试验证了 3 种锂盐  $\text{LiPF}_6$ 、二草酸硼酸锂(LiBOB)和双三氟甲磺酰亚胺锂(LiTFSI)溶于 3 种砜类溶剂环丁砜(TMS)、亚硫酸二甲酯(DMS)和亚硫酸二乙酯(DES)中形成的电解液的电化学窗口均大于 5.4 V, 且室温下离子电导率均大于 3 mS/cm, 表明砜类溶剂是非常有前景的高压溶剂. 但砜类溶剂黏度较大, 与石墨负极不兼容, 往往需加入共溶剂和负极添加剂协同作用. 如 Hilbig 等<sup>[23]</sup>发现石墨半电池(电压 0.02~1.50 V, 充放电倍率 1 C)在基础电解液 1 mol/L  $\text{LiPF}_6\text{-EMS}$  中首次循环的库伦效率为 30.2%, 是由于 EMS 在约 1.2 V (vs.  $\text{Li/Li}^+$ )处开始发生还原分解, 但分解产物不能形成有效的 SEI 膜, 故电池的库伦效率较低; 将 4wt% FEC 作为添加剂加入石墨半电池中, 相同测试条件下, 半电池的首次库伦效率提高到 80.7%, 首次放电比容量达 325 mA·h/g, 且循环 100 次后容量几乎无衰减, 原因在于 FEC 在石墨负极上的成膜作用隔离了 EMS 与石墨电极, 进而有效阻止了 EMS 还原分解.

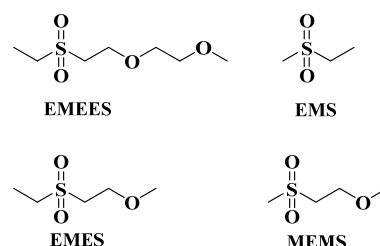


图 2 几种砜类溶剂的结构

Fig.2 The structures of several sulfone-based solvents

## 2.3 离子液体

离子液体(室温熔融盐)主要由有机阳离子和无机阴离子组成, 常见的离子液体有咪唑类、哌啶类和吡咯类等<sup>[24-26]</sup>. 离子液体作为新型有机溶剂, 具有许多独特的物化性质, 如蒸汽压低、不易燃、宽液程, 同时具有较高的热稳定性及电化学稳定性(氧化电位通常大于 5 V, vs.  $\text{Li/Li}^+$ ). 因此, 离子液体符合高压高安全电解液的标准, 近年来受到广泛关注<sup>[27-29]</sup>.

最常见的离子液体是咪唑类离子液体, 但咪唑阳离子的 C(2)具有强还原性, 使咪唑阳离子在 1.0 V (vs.  $\text{Li/Li}^+$ )电位处开始发生还原反应, 如 0.8 mol/L  $\text{LiTFSI-[EMI][TFSI]}$ (1-乙基-3-甲基咪唑双三氟甲磺酰亚胺盐)的电解液由于 1-乙基-3-甲基咪唑阳离子 $[\text{EMI}]^+$

共嵌在石墨层中还原分解,使石墨半电池无可逆容量<sup>[30]</sup>。这一问题有 3 种解决方案,一是改变阴离子结构,如将 [EMI][TFSI] 改为 [EMI][FSI] [1-乙基-3-甲基咪唑二(氟甲磺酰基)亚胺盐] 后,石墨半电池在 0.2 C 充放电倍率下循环 30 次后放电比容量为 360 mA·h/g<sup>[30]</sup>;二是取代咪唑阳离子的 C(2)<sup>[31]</sup>;三是使用成膜添加剂<sup>[32]</sup>。

Schmitz 等<sup>[33]</sup>使用 0.3 mol/L LiTFSI-[C<sub>2</sub>MIm][TFSI] (1-乙基-3-甲基咪唑双三氟甲磺酰亚胺盐), 0.3 mol/L LiTFSI-[C<sub>4</sub>MIm][TFSI] (1-丁基-3-甲基咪唑双三氟甲磺酰亚胺盐), 0.3 mol/L LiTFSI-[Pyr<sub>14</sub>][TFSI] (N-甲基-N-丁基吡咯双三氟甲磺酰亚胺盐) 三种离子液体电解液, 分别以 LiFePO<sub>4</sub> 和金属锂为正负极组装电池, 恒电流充放电结果表明, 半电池在咪唑类电解液 0.3 mol/L LiTFSI-[C<sub>2</sub>MIm][TFSI] 和 0.3 mol/L LiTFSI-[C<sub>4</sub>MIm][TFSI] 中的放电比容量不稳定且衰减很快, 循环后隔膜呈棕色; 而在吡咯类电解液 0.3 mol/L LiTFSI-[Pyr<sub>14</sub>][TFSI] 中的放电比容量稳定在 130 mA·h/g, 且库伦效率大于 99%。在咪唑类电解液中加入成膜添加剂 FEC 后, LiFePO<sub>4</sub>/Li 的容量保持率和库伦效率达到吡咯类电解液的水平, 表明吡咯类离子液体用于电解液中的性能优于咪唑类离子液体。Cao 等<sup>[34]</sup>比较了 LNMO/LTO (钛酸锂) 全电池在常规电解液 1 mol/L LiPF<sub>6</sub>-EC:DEC (质量比 1:1) 与 0.7 mol/L LiTFSI-[Pyr<sub>14</sub>][TFSI] 和 0.7 mol/L LiTFSI-[MMMPyr][TFSI] (甲基-甲基羧甲基吡咯双三氟甲磺酰亚胺盐, 结构如图 3 所示) 两种离子液体电解液中的性能, 线性伏安测试表明离子液体电解液的电化学窗口高于传统电解液, 这一现象在高温下更明显, 60 °C 下离子

液体电解液在 Pt 电极上的氧化电位为 4.5 V (vs. Li/Li<sup>+</sup>), 而常规电解液的氧化电位仅为 3.9 V (vs. Li/Li<sup>+</sup>)。LNMO/LTO 全电池的充放电测试结果表明, 60 °C 下基于常规电解液的全电池首次放电比容量仅为 38 mA·h/g, 循环 35 次后容量完全衰减; 基于离子液体电解液的全电池首次放电比容量为 105 mA·h/g, 循环 50 次后约为 70 mA·h/g。

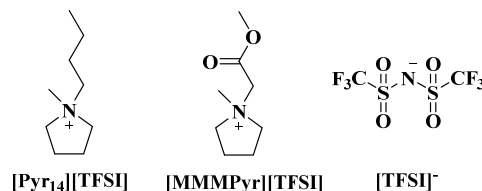


图 3 离子液体 [Pyr<sub>14</sub>][TFSI] 和 [MMMPyr][TFSI] 的结构式

Fig.3 The structures of ionic liquids [Pyr<sub>14</sub>][TFSI] and [MMMPyr][TFSI]

除以上几种溶剂外, 还有高压溶剂 (表 1), 如腈类溶剂等, 表 2 列出了高压溶剂性质的对比。

### 3 高压电解液添加剂

相比于新型高压溶剂, 高压添加剂因其用量少、效果明显、成本低而更受青睐<sup>[50]</sup>。关于添加剂的作用机理, 目前普遍观点是添加剂在正极表面氧化分解形成致密的 CEI 膜, 该膜可有效传导锂离子, 但对电子绝缘, 所以可改善高压正极与电解液间的界面稳定性, 进一步提高电池的循环稳定性。近日, Gao 等<sup>[51]</sup>分别以对二氟草酸硼酸锂 (LiDFOB) 和 3-己基噻吩 (3HT) 为代表物质, 提出高压电解液添加剂的两种不同作用原理: (1) 形成

表 1 锂离子电池高压溶剂的性能

Table 1 Performances of high-voltage solvents for lithium ion batteries

| High-voltage solvent |                                | Electrochemical system  | Discharge retention/% <sup>1)</sup>        | Ref. |
|----------------------|--------------------------------|---|--|------|
| Fluorinated          | Fluoroethylene carbonate (FEC) | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Si, 1 mol/L LiPF <sub>6</sub> -FEC:DMC (1:4, mass ratio)  | 92.2 (0.5 C, 200 cycles)                   | [35] |
|                      |                                | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li, 1 mol/L LiPF <sub>6</sub> -FEC:EMC (3:7, volume ratio)  | 100.0 (0.27 C, 106 cycles)                 | [36] |
|                      |                                | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /Li, 1 mol/L LiPF <sub>6</sub> -FEC:DMC (1:4, volume ratio)  | 82.7 (0.2 C, 100 cycles)                   | [37] |
|                      | Ethyl difluoroacetate (DFEAc)  | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub> /Li, 1 mol/L LiPF <sub>6</sub> -FEC:DFEAc (3:7, mass ratio)  | 89.2 (0.5 C, 100 cycles)                   | [38] |
| Dinitrile-based      | Adiponitrile (ADN)             | LiCoO <sub>2</sub> /Graphite, 1 mol/L LiTFSI, 0.1 mol/L LiBOB-EC:ADN (1:1, volume ratio)  | 90.0 (1/12 C, 50 cycles)                   | [39] |
|                      |                                | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /Li, 0.9 mol/L LiBF <sub>4</sub> -EC:ADN (1:1, mass ratio)   | 97.0 (0.5 C, 50 cycles)                    | [40] |
|                      | Pimelonitrile (PMN)            | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li, 1 mol/L LiBF <sub>4</sub> , 0.1 mol/L LiBOB-EC:DMC:PMN (1:1:2, volume ratio)  | 86.0 (1/12 C, 50 cycles)                   | [41] |
| Sulfone-based        | Sulfolane (SL)                 | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li, 1 mol/L LiODFB-SL:DMC (2:1, volume ratio)   | 93.0 (0.5 C, 150 cycles)                   | [42] |
|                      |                                | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li, 1 mol/L LiBF <sub>4</sub> -SL:EA (1:1, volume ratio)+2vol% VC   | 100.0 (0.5 mA/cm <sup>2</sup> , 30 cycles) | [43] |
|                      | Tetramethyl sulfone (TMS)      | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> , 1 mol/L LiPF <sub>6</sub> -TMS  | 90.0 (1/12 C, 100 cycles)                  | [44] |
| Ionic liquid         | Ethylmethyl sulfone (EMS)      | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li, 1 mol/L LiPF <sub>6</sub> -EMS:DMC (1:1, mass ratio)  | 97.8 (0.2 C, 100 cycles)                   | [45] |
|                      | [C4mpyr][TFSI]                 | Li <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> @C/Li, 1 mol/L LiTFSI-[C4mpyr][TFSI]   | 83.1 (0.1 C, 50 cycles)                    | [46] |
|                      | [C3mpyr][TFSI]                 | Li <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> @C/Li, 1 mol/L LiTFSI-[C3mpyr][TFSI]   | 84.5 (0.1 C, 50 cycles)                    | [46] |
|                      | [SN1IL][TFSI]                  | LiCoO <sub>2</sub> /graphite, 0.6 mol/L LiPF <sub>6</sub> , 0.4 mol/L LiODFB-[SN1IL][TFSI]:DMC (1:1, volume ratio)  | 99.0 (0.2 C, 90 cycles)                    | [47] |
|                      | [Py <sub>14</sub> ][TFSI]      | Li[Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> ]O <sub>2</sub> /Li, 1 mol/L LiPF <sub>6</sub> -[Py <sub>14</sub> ][TFSI]:EC:DMC (60:20:20, volume ratio) | 84.4 (1 C, 150 cycles)                     | [48] |
|                      | [PP14][TFSI]                   | Li <sub>1.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> O <sub>2</sub> /Li, 0.5 mol/L LiDFOB-[PP14][TFSI]:TMS (6:4, mass ratio)   | ~73.3 (0.1 C, 30 cycles)                   | [49] |

Note: 1) At room temperature.

表2 锂离子电池电解液常见高压溶剂的特点

Table 2 The characteristics of common high-voltage solvents for lithium ion batteries

| Solvent       | Advantage  | Disadvantage   |
|---------------|--|--|
| Sulfone-based | High oxidative voltage (>5.5 V), high dielectric constant (>40)  | High viscosity, high melting point   |
| Fluorinated   | High oxidative voltage, superior wetting ability with separator  | High viscosity, low ionic conductivity   |
| Nitrile-based | High oxidative voltage (>7 V), high flash point and non-flammable                                      | High reductive voltage and the decomposition products of reductive reaction cannot form an effective interfacial layer on the graphite anode |
| Ionic liquid  | Wide electrochemical window (4~6 V), high flash point and non-flammable, a wide diversity of structure | High viscosity, high cost, poor wetting ability with separator and electrodes  |

的 CEI 膜电子绝缘,可直接减少电解液的氧化分解;(2)一些有机物单体聚合后形成的聚合物 CEI 膜具有电子传导能力(电导率为 10~10<sup>3</sup> S/cm),其形成的 CEI 膜不能绝缘电子,但可阻止 H<sup>+</sup>或其它破坏性物质对正极材料的进攻,进而提高电池的循环稳定性。

3.1 硼类添加剂

硼类添加剂在正负极表面有优异的成膜作用<sup>[52-55]</sup>,近年来很受青睐. Cha 等<sup>[56]</sup>将 LiDFOB 用于富锂正极 Li<sub>1.17</sub>Ni<sub>0.17</sub>Mn<sub>0.5</sub>Co<sub>0.17</sub>O<sub>2</sub> 中,发现在基础电解液 1.3 mol/L LiPF<sub>6</sub>-EC:EMC:DMC(体积比 3:4:3)中加入浓度 1wt% 的 LiDFOB 后,半电池的充电比容量降低,放电比容量增加,表明库伦效率增大;半电池在 4.9 V 恒压下的极化测试结果表明,加入添加剂可减小高压下的氧化电流,表明该添加剂可抑制电解液氧化分解;循环性能测试表明,加入 LiDFOB 后, Li<sub>1.17</sub>Ni<sub>0.17</sub>Mn<sub>0.5</sub>Co<sub>0.17</sub>O<sub>2</sub>/Li 在 0.5 C 充放电倍率下循环 200 次后容量保持率为 81.4%,而在基础电解液中相同条件下循环 200 次后容量保持率仅为 12.2%. 电池循环后的 XPS, TEM, SEM 分析结果表明,有 LiDFOB 存在时,正极电极表面形成的 CEI 膜中 LiF 含量较少,该膜可有效保护正极材料结构的完整性,对石墨负极的 SEM 和 XPS 测试表明, LiDFOB 在负极还原分解,修饰负极 SEI 膜,该膜富含 LiF,且有利于锂离子脱嵌. Bian 等<sup>[57]</sup>将 LiDFOB 作为复合盐与 LiPF<sub>6</sub> 协同作用,用于以富锂材料 Li<sub>1.18</sub>Ni<sub>0.15</sub>Co<sub>0.15</sub>Mn<sub>0.52</sub>O<sub>2</sub> 为正极的纽扣半电池中,充放电测试表明,加入 LiDFOB 后电池的循环性能明显提升,常温下容量保持率从 69.4% 提高到 96%,物理表征表明加入 LiDFOB 有助于形成稳定的 CEI 膜. 除 LiBOB 和 LiDFOB 外,还有很多有前景的硼类添加剂,如 Wang 等<sup>[58]</sup>将三(2,2,2-三氟乙基)硼酸(TTFEB)用于 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/Li 中,发现加入 0.5wt% TTFEB 后 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/Li 在高倍率(4 C)下循环 100 次后放电比容量仍达 135.1 mA·h/g,而相同测试条件下,无添加剂时循环 100 次后放电比容量仅为 73.7 mA·h/g. EIS, SEM 和 TEM 分析表明,性能提升的原因在于在正极表面形成了均一、阻抗低的 CEI 膜。

3.2 苯衍生物及杂环类添加剂

苯衍生物及杂环类有机物单体通常在约 4.0 V (vs.

Li/Li<sup>+</sup>)以上的电位下发生氧化反应,形成正极保护膜,目前高压正极均要求充电至 4.0 V 以上为苯环衍生物和杂环类化合物氧化分解提供电压条件,因此近年来苯环衍生物和杂环类添加剂被广泛用于锂离子电池中. Lee 等<sup>[59]</sup>将多巴胺作为电解液添加剂用于 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/石墨全电池中,发现加入含量 0.1wt% 的多巴胺后,全电池在充放电倍率 1 C、电压 3.0~4.5 V 的条件下循环 100 次后,放电比容量和容量保持率分别为 147 mA·h/g 和 90.1%;而无添加剂的全电池在相同条件下循环 100 次后,放电比容量和容量保持率分别为 136 mA·h/g 和 83.3%. SEM 测试表明,加入添加剂后正极表面结构与循环前类似,无添加剂的电池循环后正极表面覆盖了一层很厚的电解液分解产物. X 射线光电子谱的 N 1s 峰表明,预循环后多巴胺氧化聚合为聚多巴胺,有效提高了电极和电解液的界面稳定性,进而提高了电池的循环性能. 此外, Huang 等<sup>[60]</sup>将 0.5wt% 对三氟甲基苯腈作为添加剂加入常规电解液中,发现由于对三氟甲基苯腈氧化分解形成了有效的 CEI 膜,使 LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li 循环 300 次后容量保持率提高了 16%. Wang 等<sup>[61]</sup>在高压钴酸锂(充电至 4.5 V)半电池中验证了对三氟甲基苯腈在钴酸锂正极上的成膜作用,证明对三氟甲基苯腈在高压下氧化分解形成了能保护正极材料和电解液的一层致密的 CEI 膜. 因此,苯环衍生物及杂环类添加剂是一类十分有前景的高压电解液添加剂。

3.3 亚磷酸盐类添加剂

Wang 等<sup>[62]</sup>尝试用三(2,2,2-三氟乙烷基)亚磷酸盐(TTFEP)作电解液添加剂,用于 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/Li 半电池中,由于 TTFEP 氧化分解形成稳定的 CEI 膜,使 LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/Li 在 0.5 C 充放电倍率下循环 100 次后容量保持率提高了 11.2%. Zhang 等<sup>[63]</sup>将三(三甲基硅基)磷酸酯(TMSP)作为高压添加剂用于以富锂材料 Li[Li<sub>0.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>]O<sub>2</sub> 为正极的纽扣半电池中,线性伏安测试结果表明, TMSP 的氧化电位为 4.1 V (vs. Li/Li<sup>+</sup>),低于传统碳酸酯溶剂的氧化电位;XPS 分析结果表明,CEI 膜的主要成分来自 TMSP 的氧化分解;充放电测试结果表明,加入 1wt% TMSP 后, Li[Li<sub>0.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>]O<sub>2</sub>/Li 半电池在 20 mA/g, 2.0~4.8

V 条件下循环 50 次后, 容量保持率高达 91.1%.

3.4 其它添加剂

除上述几种添加剂外, 其它类型添加剂如醚类<sup>[64]</sup>、含硫类<sup>[65]</sup>、有机硅类<sup>[66]</sup>、离子液体类<sup>[67]</sup>等添加剂也被广泛研究和应用(如表 3 所示). Tu 等<sup>[66]</sup>发现在电解液中添加 0.25wt% 三甲基硅基环戊二烯(SE)后,

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/Li 半电池在 50℃、充放电倍率 1 C 下循环 100 次后, 放电容量保持率为 88%, 但在空白电解液中相同测试条件下仅循环 75 次, 放电比容量即从 120 mA·h/g 降到 18 mA·h/g; 电化学测试和物理表征进一步证明 SE 提前氧化分解并形成了有效的 CEI 膜, 保护正极材料和电解液, 使电池的循环性能提升.

表 3 锂离子电池高压添加剂研究进展  
Table 3 The development of high-voltage additives for lithium ion batteries

| Type  | Additive   | Electrochemical system   | Voltage/V | Discharge capacity retention/% <sup>1)</sup> | Ref. |
|---|--|--|-----------|--|------|
| Boron-containing                            | Triethylborate (TEB)   | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /Li       | 3.0~4.5   | 99.8 (1 C, 150 cycles)                       | [68] |
|   | Trimethyl borate (TMB)   | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~4.9   | 85.3 (1 C, 600 cycles)                       | [69] |
| Benzene derivatives & heterocyclic compound | Terthiophene (3THP)  | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~4.9   | 91.0 (1 C, 350 cycles)                       | [70] |
|   | Glutaric anhydride (GA)  | LiNi <sub>0.5</sub> Mn <sub>0.5</sub> Co <sub>0.2</sub> O <sub>2</sub> /graphite | 3.0~4.4   | 95.2 (1/3 C, 117 cycles)                     | [71] |
|   | Thiophene  | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /MCMB     | 3.0~4.5   | 85.2 (1 C, 200 cycles)                       | [72] |
| Phosphorus-containing                       | Ethylene dioxythiophene (EDOT)                                   | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /MCMB     | 3.0~4.5   | 81.8 (1 C, 200 cycles)                       | [72] |
|   | Dimethylmethylphosphonate (DMMP)                                 | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.5~4.9   | 70.0 (0.2 C, 50 cycles)                      | [73] |
|   | Tris(2,2,2-trifluoroethyl) phosphite (TTFEP)                     | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /Li       | 3.0~4.6   | 85.4 (0.5 C, 100 cycles)                     | [74] |
|   | Tris(trimethylsilyl) phosphite (TMSPi)                           | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /Li       | 3.0~4.5   | 91.2 (0.5 C, 100 cycles)                     | [75] |
| Sulfur-containing                           | Di(methylsulfonyl) methane (DMSM)                                | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /graphite | 3.0~4.6   | 80.1 (0.2 C, 100 cycles)                     | [65] |
|   | P-Toluenesulfonyl isocyanate (PTSI)                              | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub> /Li       | 3.0~4.5   | 82.6 (1 C, 100 cycles)                       | [76] |
|   | Methylene methanedisulfonate (MMDS)                              | LiCoO <sub>2</sub> /graphite   | 3.0~4.5   | 69.6 (1 C, 150 cycles)                       | [77] |
|   | 1,1'-Sulfonyldiimidazole (SDM)                                   | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~4.9   | 96.9 (1 C, 100 cycles)                       | [78] |
| Organosilicone                              | Phenyl trifluoromethyl sulfide (PTS)                             | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~4.9   | 84.0 (1 C, 450 cycles)                       | [79] |
|   | Tris(trimethylsilyl)borate (TMSB)                                | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~5.0   | 85.0 (1 C, 600 cycles)                       | [80] |
|   | Tris(trimethylsilyl)phosphate (TMSP)                             | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.0~5.0   | 71.0 (1 C, 600 cycles)                       | [80] |
|   | Allyloxytrimethylsilane (AMSL)                                   | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> /Li                         | 3.5~5.0   | 80.2 (1 C, 500 cycles)                       | [81] |
| Carbonate                                   | 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetra-siloxane (ViD4) | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> /Li       | 3.0~4.5   | 83.6 (1 C, 150 cycles)                       | [82] |
|   | Vinyl ethylene carbonate (VEC)                                   | LiNi <sub>0.4</sub> Mn <sub>0.4</sub> Co <sub>0.2</sub> O <sub>2</sub> /graphite | 3.0~4.5   | 74.5 (1 C, 300 cycles)                       | [83] |
|   | Methyl 3,3,3-trifluoropropanoate (TFPM)                          | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /graphite | 3.0~4.6   | 75.4 (0.2 C, 100 cycles)                     | [84] |
|   | Ethyl 3,3,3-trifluoropropanoate (TFPE)                           | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub> /graphite | 3.0~4.6   | 76.1 (0.2 C, 100 cycles)                     | [84] |

Note: 1) At room temperature.

4 高浓电解液

非质子性溶剂在低电压(约 0 V, vs. Li/Li<sup>+</sup>)附近易发生还原分解反应, 仅有少数特殊溶剂如 EC 分解后可形成有效的 SEI 膜, 因而近年来 EC 几乎一直是锂离子电池电解液的必要组成部分. 但 EC 黏度大, 需将其与黏度小的溶剂如 DMC, DEC 和 EMC 等混合作为电解液溶剂. 同时 LiPF<sub>6</sub>因具有离子电导率较高、可钝化 Al 集流体等优点, 成为商业化锂离子电池的锂盐. 基于以上原因, 传统电解液的组成相对固定, 即 1 mol/L LiPF<sub>6</sub>溶解于 EC, DMC 和 DEC 等碳酸酯溶剂中. 但传统电解液溶剂电压大于 4.3 V (vs. Li/Li<sup>+</sup>)时易发生氧化分解反应, 且 LiPF<sub>6</sub>遇痕量水或高温下易分解产生 HF, 破坏电极结构, 因而无法满足高压高安全电解液的要求. Suo 等<sup>[85]</sup>发现超高浓度的锂盐水溶液具有良好的电化学稳定性, 可作为锂离子电池的电解液, 提出了高浓锂盐电解液的概念, 即电解液中锂盐浓度高(一般在 3 mol/L 以上), 使该电解液体系具有不一般的性质, 如优异的耐氧化/还原能力、可预防铝集流体腐蚀、提高电池的倍率性能等. 后续叙述的高浓锂盐电解液均为有机溶剂中的

电解液体系.

醚类化合物的 HOMO 能级高, 易氧化分解, 可用作高压电解液添加剂, 但不适合用作锂离子电池高压溶剂. 但醚类溶剂中氧原子的孤对电子与锂离子的相互作用使醚类溶剂对锂盐有很强的溶解能力. Yoshida 等<sup>[86]</sup>应用这一优势, 分别用三乙二醇二甲醚(G3)和四乙二醇二甲醚(G4)作溶剂, 研究醚类溶剂作为锂离子电池高压电解液溶剂的可能性. 线性伏安测试表明, [Li(G3/G4)<sub>x</sub>][TFSI]的氧化电位随锂盐浓度增大即 x 减小而逐渐增大, 当 x=1 时[Li(G3/G4)][TFSI]的氧化电位高达 5.3 V (vs. Li/Li<sup>+</sup>); Ab initio 分子轨道计算结果表明, x=1 时, 醚类溶剂与锂离子形成复合阳离子 [Li(G3/G4)]<sup>+</sup>, 使醚类分子中氧原子的孤对电子转向锂离子, HOMO 能级降低, 提高了电解液的氧化稳定性; 充放电测试结果表明, 稀电解液(x=4)时, LiCoO<sub>2</sub>/Li 半电池的容量衰减很快, x=1 时容量保持率有较大提升, Li/[LiG<sub>3</sub>][TFSI]/LiCoO<sub>2</sub> 以 0.125 C 充放电倍率循环 10 次后, 放电比容量约为 20 mA·h/g; 在相同测试条件下 Li/[LiG<sub>3</sub>][TFSI]/LiCoO<sub>2</sub> 半电池循环 200 次后放电比容量仍高达 100 mA·h/g. 这是首次将醚类溶剂用作 4 V 级



电池电解液溶剂并成功循环 200 次的报道,证实了高浓锂盐可提高电解液的耐氧化能力。

Doi 等<sup>[87]</sup>以  $\text{LiPF}_6$  为锂盐,碳酸丙烯酯(PC)为溶剂,考察高浓锂盐电解液在高压正极  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  上的稳定性,随锂盐浓度提高,电解液在 Pt 电极上的氧化稳定性增加。恒电流充放电测试表明,LNMO/Li 半电池在稀(0.83 mol/kg)电解液  $\text{LiPF}_6/\text{PC}$  中首次循环放电比容量为 128 mA·h/g,循环 50 次后容量保持率为 79.5%;而在高浓(4.27 mol/kg)电解液  $\text{LiPF}_6/\text{PC}$  中循环 50 次后放电比容量为 122.8 mA·h/g,容量保持率为 92.3%,表明提高锂盐浓度可提高电解液的氧化稳定性,进一步提高电池的循环稳定性。

腈类溶剂的 HOMO 能级低,耐氧化性能优异,但其还原稳定性差,且难与石墨负极形成良好的 SEI 膜,阻碍了其实际应用。Yamada 等<sup>[88]</sup>尝试用高浓锂盐提高腈类溶剂的还原稳定性,在 1 mol/L  $\text{LiTFSI}$ /乙腈(AN)电解液中,乙腈与锂反应,锂片溶解,因此该浓度下乙腈不能用于锂金属电池或以石墨为负极的锂离子电池

中;但当锂盐浓度提高到 4.2 mol/L 时,乙腈不再与锂反应,这为乙腈在锂离子电池中的应用提供了前提。纯乙腈溶剂的拉曼光谱在  $2258\text{ cm}^{-1}$  处有特征峰,随锂盐浓度增大,该峰强度减弱,与锂离子溶剂化的乙腈分子的特征峰( $2282\text{ cm}^{-1}$ )强度增大,锂盐浓度达 4.2 mol/L 时, $2258\text{ cm}^{-1}$  处的特征峰消失,仅剩  $2282\text{ cm}^{-1}$  处的特征峰,表明此时没有单独的乙腈分子存在;而在稀(1 mol/L)电解液中,分别有  $[\text{TFSI}]^-$ 、接触离子对 CIP ( $[\text{TFSI}]^-$  与 1 个  $\text{Li}^+$  结合)和离子集合体 AGG ( $[\text{TFSI}]^-$  与多个  $\text{Li}^+$  结合)三个特征峰;锂盐浓度为 4.2 mol/L 时,所有的  $[\text{TFSI}]^-$  均以强库伦相互作用力与锂离子结合为 AGG 状态,无独立存在的  $[\text{TFSI}]^-$ 。如图 4 所示,Yamada 等<sup>[89]</sup>认为高浓锂盐电解液优异的还原稳定性是由于 AGG 状态下的  $[\text{TFSI}]^-$  中氧原子的孤对电子偏向锂离子,使其 LUMO 能级降低,易发生还原反应形成 SEI 膜,同时由于高浓电解液中没有单独的溶剂分子存在,使电解液对 SEI 膜的溶解能力下降,因此提高了高浓电解液的还原稳定性。

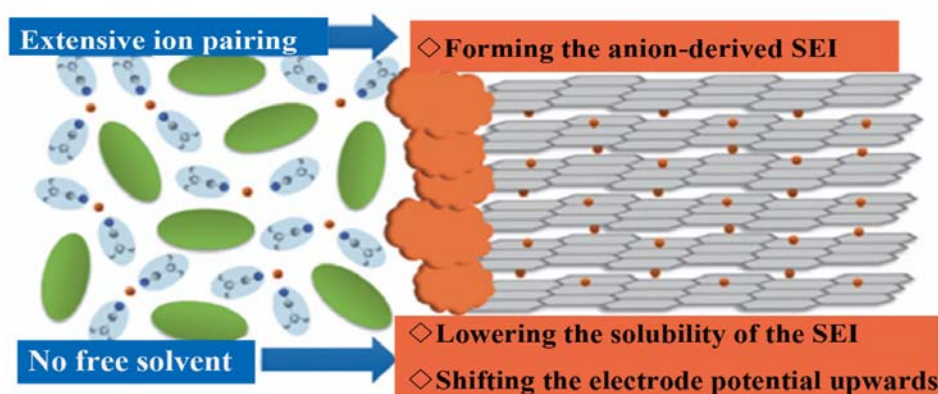


图 4 高浓电解液  $\text{LiTFSI}/\text{AN}$  的特殊结构及其还原稳定性示意图<sup>[89]</sup>

Fig.4 The unique structure of superconcentrated electrolytes and the schematic diagram of their reductive stability<sup>[89]</sup>

此外,新型锂盐如  $\text{LiTFSI}$ 、双氟酰胺亚胺锂( $\text{LiFSI}$ )等由于热稳定性好、对水分不敏感而备受关注,但这类锂盐无法钝化 Al 集流体,高电压下 Al 集流体明显腐蚀而无法快速推广使用,原因在于稳定的化学结构使其无法与 Al 集流体反应生成  $\text{AlF}_3$  保护膜。因此,为了同时保护正极材料和 Al 集流体,研发既不形成 HF、又可有效钝化 Al 集流体的新电解液体系尤为关键。

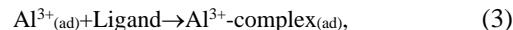
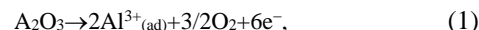
Wang 等<sup>[90]</sup>发现用高浓锂盐电解液体系  $\text{LiFSI}:\text{DMC}$  (摩尔比 1:1.1)可完美解决这一困境。 $\text{LiFSI}$  结构稳定,不产生 HF,不会破坏正极材料结构,且高浓锂盐电解液可有效钝化 Al 集流体。线性伏安测试表明,随锂盐浓度增加,Al 集流体的氧化电位增加,当摩尔比  $\text{LiFSI}:\text{DMC}$  达 1:1.1 时,Al 集流体的氧化电位达 5.7 V,且氧化电流

很小;充放电循环测试表明,稀电解液情况下,由于 Al 集流体被腐蚀,使其与 LNMO 正极的接触变差,导致性能迅速衰减,如 LNMO 半电池在摩尔比  $\text{LiFSI}:\text{DMC}=1:10.8$  的电解液中由于集流体被腐蚀,无法实现首次充电,在摩尔比  $\text{LiFSI}:\text{DMC}=1:1.9$  的电解液中在 0.2 C 充放电倍率下循环 50 次后,放电比容量由约 105 mA·h/g 衰减至 25 mA·h/g;而摩尔比  $\text{LiFSI}:\text{DMC}=1:1.1$  的高浓锂盐电解液在相同测试条件下循环 100 次后容量保持率为 95%,库伦效率接近 100%。

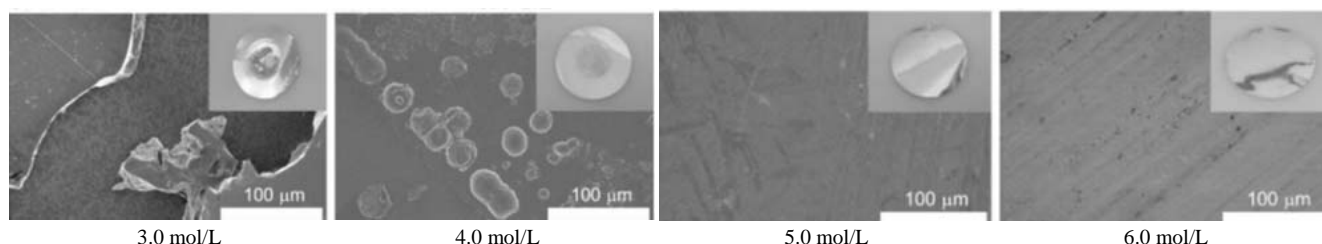
Yamada 等<sup>[91]</sup>将 Al 集流体在 4.5 V 电位下极化 10 h,Al 集流体在 3.0 和 4.0 mol/L  $\text{LiFSI}/\text{AN}$  电解液中腐蚀严重,表面形成许多小洞[图 5(a)];而在 5.0 和 6.0 mol/L  $\text{LiFSI}/\text{AN}$  的电解液中,Al 集流体表面无明显变化,与

图 5(b)所示的计时电流测试结果相同,均表明高浓锂盐电解液可抑制 Al 集流体腐蚀;恒电流充放电测试结果[图 5(c)]表明,  $\text{LiMn}_2\text{O}_4/\text{Li}$  半电池在 3.0 mol/L LiFSI/AN 电解液中的放电容量迅速衰减,而在 5.0 和 6.0 mol/L LiFSI/AN 电解液中容量几乎无衰减,且库伦效率接近 100%。高浓电解液抑制 Al 集流体腐蚀的原因为,Al 集流体腐蚀分为 4 步[式(1)~(4)],在稀电解液中,由于存在许多单独的溶剂分子,反应(3)迅速进行,且由于浓度梯度使扩散条件良好,反应(4)亦迅速进行,因而裸露出 Al 集流体,导致反应(1)和(2)继续进行,循环往复,造成 Al 集流体严重腐蚀;但在高浓电解液中,由于没有

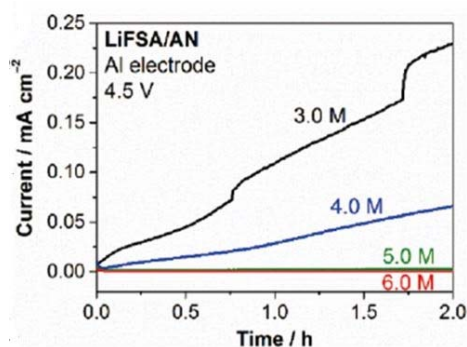
单独的溶剂分子存在,阻碍了反应(3)进行,且高浓电解液对  $\text{Al}^{3+}$  复合化合物的溶解能力较差,使反应(4)溶解及扩散较难进行,保护了 Al 集流体。



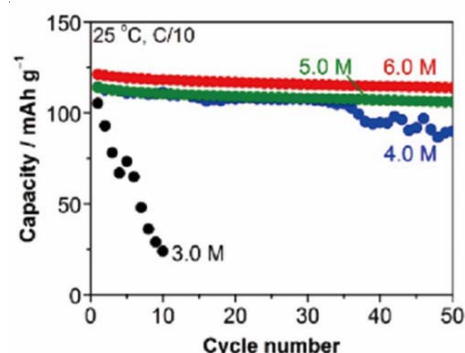
式中,下标 ad 代表吸附在 Al 集流体上, sol 代表溶解在电解液中, Ligand 为路易斯碱,如溶剂分子和阴离子。



(a) SEM images of the Al electrode surface kept at 4.5 V for 10 h in various concentrations LiFSI/AN electrolytes



(b) Chronoamperograms of Al electrode in LiFSI/AN electrolyte



(c) Discharge capacity of  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells in LiFSI/AN electrolyte

图 5 Al 集流体在 4.5 V 电位下极化 10 h 后的 SEM 图和在 不同浓度 LiFSI/AN 电解液中的计时电流图、 $\text{LiMn}_2\text{O}_4/\text{Li}$  半电池在不同浓度 LiFSI/AN 电解液中的放电比容量<sup>[91]</sup>

Fig.5 SEM images of the Al electrode surface kept at 4.5 V for 10 h in LiFSI/AN electrolyte, chronoamperograms of the Al electrode in various LiFSI/AN electrolytes at 4.5 V, discharge capacity of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells in various LiFSI/AN electrolytes<sup>[91]</sup>

## 5 结语与展望

锂离子电池电解液起着在正负极间传导锂离子的作用,是锂离子电池的重要组成部分.近年来,随着高压正极材料的不断研发,高能量密度锂电池新体系的主要挑战在于发展高压高安全的电解液.高压高安全电解液体系必须同时满足以下几方面的要求:(1)电化学窗口宽,即在较宽的电压范围内不发生氧化还原反应;(2)能在锂离子电池正负极材料表面形成稳定的固体电解质界面膜,该膜能在高压下稳定存在且能有效阻止电解液与电极材料之间的副反应;(3)良好的热稳定性,以

保证电池的安全性;(4)化学稳定性好,不与正负极材料、隔膜材料等电池附件发生化学反应;(5)绿色环保、毒性小、价格便宜.近年来,不易燃的耐高压溶剂如离子液体、砜类溶剂等被广泛研究,与此同时,高压添加剂如硼类添加剂、亚磷酸盐类添加剂等用于稳定电极/电解液界面的化合物也发展迅速.这些进步为未来锂离子电池实用型高压电解液的发展奠定了坚实的基础.但目前高压电解液仍面临诸多挑战,未来可从以下方面重点研究:

(1) 高压溶剂具有较宽的电化学窗口,但存在粘度高、与隔膜浸润性不好、与石墨负极不兼容等问题,商



业化应用仍有较大难度。目前主要使用高压溶剂与传统碳酸酯溶剂混合的多元溶剂体系以改善其黏度及其与石墨负极的相容性,但传统碳酸酯溶剂易氧化分解。因此,开发黏度较低的耐高压溶剂及能与耐高压溶剂匹配的负极添加剂是未来高压电解液研究的重要方向之一。

(2) 使用少量高压添加剂可显著提升电池的循环稳定性,因使用量较小,对电解液体系的负面影响较小,既经济又有效。但常规高压添加剂不能同时满足电解液耐高压、耐高温、耐低温、防过充及阻燃等要求,同时引入多种添加剂则可能存在不兼容、降低某方面性能等问题。因此发展多功能添加剂如阻燃高压添加剂、防过充高压添加剂等是未来高压电解液添加剂的重要研究方向之一。

高浓锂盐电解液具有常规浓度电解液不具备的特殊性质,如较强的耐氧化/还原能力、高热稳定性、低挥发性等。但其黏度较大,离子电导率低,且锂盐价格昂贵,使其商业化应用面临诸多挑战。因此,发展具有稳定化学结构且价格便宜的锂盐是未来高浓电解液发展的重要方向之一,与此同时,发展与高浓电解液匹配的溶剂体系也是未来的重要课题。

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