



### New understanding of the role of lithium nitrate additives in lithium-sulfur batteries

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# 硝酸锂添加剂在锂硫电池中作用的新理解

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摘要 硝酸锂(LiNO<sub>3</sub>)作为锂硫(Li-S)电池电解液添加剂获得了广泛的关注,对其作用机理也进行了深入研究.本研 究通过新的实验方案,对LiNO<sub>3</sub>添加剂的作用机理提出了新的理解.该实验方案中,利用含LiNO<sub>3</sub>添加剂电解液循 环过的锂金属负极和新的硫电极,与不含LiNO<sub>3</sub>添加剂电解液重新组装电池.该电池在充电过程中却存在严重过充 现象,发生了多硫离子的穿梭.这说明LiNO<sub>3</sub>抑制"穿梭效应"的作用机制不仅是生成固体电解质界面膜(solid electrolyte interphase,简称SEI膜);而且通过离子迁移数测试,发现加入LiNO<sub>3</sub>添加剂后,锂离子(Li<sup>+</sup>)迁移数增加.由此 得出,加入LiNO<sub>3</sub>添加剂的另一个作用是增加Li<sup>+</sup>迁移数,从而降低多硫离子迁移数,有效抑制"穿梭效应".

关键词 硝酸锂, 锂硫电池, 锂离子迁移数, 穿梭效应

锂硫(Li-S)电池是下一代电池体系中的候选者, 其理论能量密度可达到2600 Wh kg<sup>-1[1,2]</sup>.其中,硫正 极具有较高的比容量(单质硫的理论比容量高达1675 mAh g<sup>-1</sup>),并且硫的储存量丰富、价格低廉、对环境 友好<sup>[3,4]</sup>.然而,多硫化锂"穿梭效应"导致了电池循环 性能差、容量衰减快和过充等问题<sup>[5]</sup>,从而严重制约 了Li-S电池进一步发展和商业化应用.

2008年, Manthiram等人<sup>[6]</sup>揭示了LiNO<sub>3</sub>在抑制多 硫离子穿梭中的功效, 使Li-S电池的库仑效率接近 100%. 另外, 还发现引入LiNO<sub>3</sub>可以同时提高正极中硫 的利用率. 令人鼓舞的结果使LiNO<sub>3</sub>成为最重要的电解 液添加剂, 几乎出现在之后每一个报道的Li-S电池电解 液中. 采用LiNO<sub>3</sub>作为Li-S电池电解液添加剂是抑制 "穿梭效应"的强有力武器, 可以一定程度上满足对Li-S 电池容量和循环稳定性的需求. 根据普遍的理解, LiNO<sub>3</sub>的功能是通过自发的还原反应在锂金属负极上

形成电绝缘层,阻止多硫化物在锂负极上的进一步还 原<sup>[6]</sup>. Xiong等人<sup>[7,8]</sup>提出LiNO3与锂金属反应生成固态 Li<sub>x</sub>NO<sub>y</sub>,在负极表面形成坚固的、具有钝化负极活性 和保护负极的固体电解质界面膜(solid electrolyte interphase, 简称SEI膜). 钝化层由Aurbach等人<sup>[9]</sup>使用傅立叶 变换红外(FTIR)光谱和X射线光电子能谱(XPS)鉴定为 Li,NO,: 后来, Liang等人<sup>[10]</sup>报道了LiNO3诱导在锂负极 上形成光滑且致密的SEI层, 该层充当还原性锂金属的 保护层. 受这些有希望结果的启发, 大量精力投入到Li-S 电池的纳米结构硫正极开发研究上、从而揭示了许多 有趣的材料和发现. 尽管如此, Amine小组<sup>[11]</sup>的研究工 作表明,氧化还原穿梭抑制与Li,NO,层无关,引发了对 未来Li-S电池开发的新思考. 与此观点相呼应的另一个 相关现象是在锂负极上LiNO3持续被还原的发现, 这表 明Li<sub>x</sub>NO<sub>y</sub>层在防止多硫离子还原方面没有发挥作用<sup>[12]</sup>. 后来, Zhang<sup>[13]</sup>就充放电过程进行了深入研究, 提

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论文

出LiNO<sub>3</sub>具有催化活性, 能够在充电过程即将结束时催 化多硫化锂转化为单质硫, 并且电解液中的可溶性硝 酸盐与硫电极上的不溶性硝酸盐的结合可导致协同改 善. Shim等人<sup>[14]</sup>研究了LiNO<sub>3</sub>在不可逆产物形成中的 作用, 提出利用2.9 V以上的电势, 不可逆产物可以部 分转换为高阶多硫化物和单质S<sub>8</sub>. Sun等人<sup>[15]</sup>评估了含 LiNO<sub>3</sub>电解液的锂硫电池自放电性能, 提出使用纳米尺 寸氧化铝涂层微孔膜和含LiNO<sub>3</sub>电解液可有效抑制自 放电. 所有这些明确地证明了重新研究LiNO<sub>3</sub>在Li-S电 池中作用的必要性.

本研究利用含LiNO<sub>3</sub>添加剂电解液循环过的锂金 属负极和新的硫电极,与不含LiNO<sub>3</sub>添加剂电解液重新 组装电池,该电池在充电过程中却存在严重过充现象, 发生了多硫离子的穿梭.这说明LiNO<sub>3</sub>抑制"穿梭效应" 的作用机制不仅是生成SEI膜,与前人报道一致<sup>[16,17-26]</sup>. 为了进一步理解LiNO<sub>3</sub>在Li-S电池中的作用,通过测量 锂离子(Li<sup>+</sup>)迁移数,发现加入LiNO<sub>3</sub>添加剂后,Li<sup>+</sup>迁移 数增加.由此得出,LiNO<sub>3</sub>作为Li-S电池电解液添加剂 抑制"穿梭效应"可能与增加Li<sup>+</sup>迁移数,降低阴离子迁 移数和降低多硫阴离子迁移数有关.

# 1 实验

(i) 硫正极制备. 首先, 按照质量比为7:3准确称量 升华硫(S)与Super P, 将称量的S和Super P在玛瑙研钵 里研磨30 min. 接着, 将研磨均匀的S和Super P在氩气 气氛下升温到155°C保持10 h, 得到S和Super P复合物 (S-SP复合物). 最后, 按照质量比为9:1将S-SP复合物与 黏接剂聚偏氟乙烯(PVDF)、*N*-甲基吡咯烷酮(NMP)为 溶剂配置5%的PVDF, 瓶磨制浆, 得到的浆料均匀涂覆 到铝箔集流体上. 真空烘箱中60°C干燥12 h待用. 硫负 载量约为1.0 mg cm<sup>-2</sup>.

(ii)材料表征.用扫描电子显微镜(SEM, Hitachi S-

4800)表征样品的形貌. X射线能谱(EDS)分析样品表面 元素的分布.

(iii) 电化学性能表征.采用CR2016壳式电池进行 电化学性能表征.以S-SP复合物为硫电极,电解液采用 1 mol  $L^{-1}$ 双三氟甲烷磺酰亚胺锂(LiTFSI)的乙二醇二 甲醚(DME)和二氧戊环(DOL)(体积比1:1)的混合溶液, 含LiNO<sub>3</sub>添加剂的电解液中LiNO<sub>3</sub>浓度为2%, Celgard 2400(美国Celgard公司),在手套箱中组装电池.采用新威 电池测试系统(深圳新威新能源技术有限公司)对Li-S 电池电化学性能进行评估,电流密度为200 mA g<sup>-1</sup>,充 放电电压范围为1.8~2.8 V.

经过10个充放电循环后,在氩气气氛手套箱中将 电池拆开,取出锂金属负极和硫电极,用不含LiNO<sub>3</sub>添 加剂的电解液反复冲洗、压平、晾干24 h后,再重新与 新的对电极组装电池进行充放电测试.

在氩气气氛手套箱中,采用手术刀拉划的方法将 新的锂金属负极表面氧化膜刮去,在2% LiNO<sub>3</sub>添加剂 的电解液中浸泡6 h,用不含LiNO<sub>3</sub>添加剂电解液反复 冲洗,晾干24 h,压平后与新的硫电极组装电池进行充 放电测试.采用界面法测定Li<sup>+</sup>的迁移数(*t*L<sup>+</sup>).

# 2 结果与讨论

为了进一步研究LiNO<sub>3</sub>添加剂在Li-S电池中的作 用, 先明确和验证LiNO<sub>3</sub>添加剂的作用是否在锂金属负 极表面形成SEI层, 如图1所示. 首先, 采用含LiNO<sub>3</sub>添加 剂电解液组装Li-S电池, 进行充放电测试; 然后, 将循环 后电池拆开, 取锂金属负极与新的硫正极和不含LiNO<sub>3</sub> 添加剂电解液组装Li-S电池, 相同条件下进行充放电测 试, 看是否过充. 如果没有过充, 证明LiNO<sub>3</sub>添加剂抑制 "穿梭效应"的作用机制是因为在锂金属负极上形成 SEI膜; 如果过充, 证明LiNO<sub>3</sub>添加剂抑制"穿梭效应"的 作用机制另有原因.



图 1 LiNO<sub>3</sub>作用验证示意图 Figure 1 Schematic diagram of lithium nitrate function verification

图2为Li-S电池恒流充放电曲线.图2(a)为新的锂金 属负极与新的硫电极和含2%LiNO<sub>3</sub>添加剂电解液的首 圈、第二圈充放电曲线.首圈充电比容量为593.649 mAh g<sup>-1</sup>,放电比容量为636.671 mAh g<sup>-1</sup>,库伦效率为 93.24%;第二圈充电比容量为500.693 mAh g<sup>-1</sup>,放电比 容量为508.416 mAh g<sup>-1</sup>,第二圈库伦效率保持在 98.48%,没有明显过充现象.这与以前的研究一致,说 明含LiNO<sub>3</sub>添加剂电解液在充放电循环过程中可以有 效抑制多硫化锂的"穿梭效应".

将循环10圈后的电池在手套箱中拆开,取出锂金 属负极和硫电极,然后用不含LiNO<sub>3</sub>添加剂电解液反复 冲洗、压平、晾干24 h. 用循环后的硫电极与新的锂金 属负极和2% LiNO<sub>3</sub>添加剂电解液重新组装电池测试, 其充放电曲线如图2(b)所示. 首圈充电比容量为282.9 mAh g<sup>-1</sup>, 放电比容量为37.7 mAh g<sup>-1</sup>, 放电比容量比 较低是由于循环后硫电极中活性物质主要以多硫化锂 中间体存在, 自放电比较严重而造成的. 第二圈充放电 比容量恢复正常, 分别为281.4和280.7 mAh g<sup>-1</sup>, 库伦效 率为100.24%, 接近100%, 没有明显过充现象. 图2(c)为 循环10圈后的锂金属负极与新的硫电极及不含LiNO<sub>3</sub> 添加剂电解液重新组装电池的充放电曲线. 由图可见 首圈充电比容量为758.5 mAh g<sup>-1</sup>, 放电比容量为678.6 mAh g<sup>-1</sup>, 库伦效率为111.77%, 存在过充现象. 第二圈 充电比容量为776.6 mAh g<sup>-1</sup>, 放电比容量为701.7 mAh g<sup>-1</sup>, 第二圈库伦效率为110.67%, 仍存在过充现象. 通过 图2(b), (c)的充放电曲线可以说明, LiNO<sub>3</sub>添加剂抑制 "穿梭效应"的作用机制不全是因为在锂金属负极上形 成SEI膜, 可能还有其他作用机制.



**图 2** 恒流充放电曲线. (a) 新的锂金属负极与新的硫电极和含2% LiNO<sub>3</sub>添加剂电解液的充放电曲线; (b) 新的锂金属负极与循环10圈后的硫电 极与含2% LiNO<sub>3</sub>添加剂电解液的充放电曲线; (c) 循环后的锂金属负极与新的硫电极和不含LiNO<sub>3</sub>添加剂电解液的充放电曲线; (d) 浸泡6 h的锂 金属负极和新的硫电极与不含LiNO<sub>5</sub>添加剂电解液的充放电曲线

**Figure 2** Constant current charge-discharge curve. (a) Charge and discharge curves of fresh lithium metal anode, fresh sulfur electrode and electrolyte containing 2% LiNO<sub>3</sub> additive; (b) charge and discharge curves of fresh lithium metal anode, sulfur electrode circulating 10 cycles and electrolyte containing 2% LiNO<sub>3</sub> additive; (c) charge and discharge curve of the circulated lithium metal anode, the fresh sulfur electrode and electrolyte without LiNO<sub>3</sub> additive; (d) charge and discharge curve of the lithium metal anode after soaking for 6 h, fresh sulfur electrode and electrolyte without LiNO<sub>3</sub> additive

为了避免拆电池过程中应力对锂金属负极表面 SEI膜的影响、使实验结果更有说服力、进一步设计了 新实验验证LiNO3添加剂作用是否是在锂金属负极表 面形成SEI膜.采用含2% LiNO3添加剂电解液将锂金属 负极浸泡6h,晾干后,与新的硫电极和不含LiNO<sub>3</sub>添加 剂电解液重新组装电池,进行充放电测试.首先,如图3 锂金属负极浸泡前后表面SEM图所示,含LiNO3电解液 浸泡后, 锂金属负极表面变粗糙; 如图4所示, 浸泡后粗 糙的表面中含有N元素、结合前人提出的LiNO3与锂金 属反应生成Li,NO,固体电解质界面膜(SEI)<sup>[9,10,24]</sup>,说明 表面的粗糙物质是LiNO<sub>3</sub>添加剂在锂金属负极表面被 还原生成的SEI膜. 浸泡后, 锂金属负极组装的Li-S电池 的首圈充电比容量为718.9 mAh g<sup>-1</sup>, 放电比容量为 527.6 mAh g<sup>-1</sup>, 库伦效率为136.26%, 存在明显的过充 现象(图2(d)). 第二圈充电比容量为809.048 mAh g<sup>-1</sup>, 放 电比容量分别为699.7 mAh g<sup>-1</sup>, 库伦效率为115.63%, 仍存在明显过充现象.这与上述实验现象一致.因此, LiNO<sub>3</sub>作为锂硫电池电解液添加剂抑制"穿梭效应"仍 然存在其他未知的机理,需要进一步研究.

为了进一步探索LiNO<sub>3</sub>添加剂在Li-S电池中的作 用,对含与不含LiNO<sub>3</sub>添加剂的电解液进行了Li<sup>+</sup>迁移 数( $t_{1,i}$ )测定:

$$t_{\text{Li}^{+}} = \frac{I_{s}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{s}R_{s})},$$
(1)

式中,  $t_{Li}$ ,  $b_{Li}$ ,  $b_{Li}$ ,  $b_{Li}$ ,  $b_{Li}$ ,  $h_{0}$ 为极化前的 Li<sup>+</sup>迁移阻抗,  $R_{s}$ 为极化后的Li<sup>+</sup>迁移阻抗,  $I_{0}$ 为初始电流,  $I_{s}$ 为稳定电流.

图5所示为含2% LiNO<sub>3</sub>添加剂电解液与不含LiNO<sub>3</sub> 添加剂电解液的Li<sup>+</sup>迁移数测试结果. 将图5中的测试结 果带入式(1)得到如表1所示的结果. 从表中发现, 不含 LiNO<sub>3</sub>添加剂的电解液中 $t_{11}$ =0.2304, 含2% LiNO<sub>3</sub>的电 解液t<sub>11</sub>= 0.4812, 含2% LiNO3的电解液t<sub>11</sub>+明显增大. 离 子迁移数是离子移动电流占总电流的比例,因此,阴阳 离子的迁移数之和是1, t<sub>11</sub>-增大代表阴离子的迁移数变 小,阴离子移动变少.同时,Ding等人<sup>[27]</sup>通过Li<sub>2</sub>S<sub>6</sub>与电 解液中纯石墨和表面覆盖了NO3<sup>-</sup>石墨的吸附能计算,发 现可溶性高阶多硫离子和NO3<sup>-</sup>之间存在强相互作用,并 吸附在碳基材料上. Wang等人<sup>[28]</sup>也在石墨烯氧化物的 研究中报道过类似的情况、指出了这种明显的强结合 力.结合Ding等人<sup>[27]</sup>和Wang等人<sup>[28]</sup>的发现,可以推断, 电解液中加入LiNO3后,阴离子迁移数的减小多数归结 于多硫阴离子的迁移数减小,从而多硫离子"穿梭效应" 得到有效抑制.

# 3 结论

本工作利用含LiNO<sub>3</sub>添加剂电解液循环过的锂金 属负极与新的硫电极和不含LiNO<sub>3</sub>添加剂电解液重新 组装电池,进行恒流充放电测试发现充电过程中仍然 存在严重过充现象,验证了LiNO<sub>3</sub>添加剂抑制"穿梭效 应"的作用机制不仅是因为在锂金属负极上形成SEI膜. 通过测量Li<sup>+</sup>迁移数,发现含LiNO<sub>3</sub>的电解液*t*<sub>Li</sub>+明显增 大,从而导致多硫阴离子的迁移明显减少.因此,可以 推测LiNO<sub>3</sub>添加剂抑制"穿梭效应"的机制可能与Li<sup>+</sup>迁 移数有效增加有关.目前Li-S电池中集聚了火药的成分



图 3 锂金属负极表面SEM图. (a) 新的锂金属负极表面; (b) 含硝酸锂电解液浸泡6 h的锂金属负极表面 Figure 3 SEM images of lithium metal anode surface. (a) Fresh lithium metal anode surface; (b) lithium metal anode surface after soaked for 6 h



图 4 含硝酸锂电解液浸泡6 h后的锂金属负极表面的元素映射. (a) 锂金属负极表面; (b) 锂金属负极表面含N元素; (c) 锂金属负极表面含F元素; (d) 锂金属负极表面含O元素

Figure 4 The element mapping diagram of the surface of lithium metal anode after immersing in lithium nitrate electrolyte for 6 h. (a) The surface of lithium metal anode; (b) the surface of the lithium metal contains N element; (c) the surface of the lithium metal anode contains F element; (b) the surface of the lithium metal anode contains O element



图 5 含2% LiNO<sub>3</sub>添加剂(a)和无LiNO<sub>3</sub>添加剂(b)电解液的Li<sup>+</sup>迁移数测试结果 Figure 5 The relationship between the ion migration current and time in the electrolyte containing 2% LiNO<sub>3</sub> additive (a) and without LiNO<sub>3</sub> additive (b)

#### 表1 实验参数表

Table 1 Parameters of experience

样品	$\Delta V(mV)$	$R_0$	$I_0(mA)$	R <sub>s</sub>	$I_{\rm s}$	$I_{o}R_{o}$	$I_{\rm s}R_{\rm s}$	Li <sup>+</sup> 迁移数
无LiNO3	10	77.5	0.126	80.4	0.113	9.765	9.0852	0.2304
有LiNO <sub>3</sub>	10	58.6	0.163	61.4	0.149	9.5518	9.1486	0.4812

(硫、硝、碳), 在商业化使用过程中可能存在潜在的危险. 根据本工作对LiNO<sub>3</sub>添加剂在Li-S电池中作用的新发现, 在未来的研究工作中可以根据迁移数理论, 寻找

能促进锂离子迁移数和与多硫离子有相互作用的其他 电解液添加剂替代LiNO<sub>3</sub>添加剂,从而降低Li-S电池在 使用中的潜在危险.

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Summary for "硝酸锂添加剂在锂硫电池中作用的新理解"

# New understanding of the role of lithium nitrate additives in lithium-sulfur batteries

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Lithium-sulfur (Li-S) batteries are considered to be one of the next-generation battery candidates and have been widely studied. Despite the obvious advantages of Li-S batteries, there are still many serious problems with sulfur electrode: The active material sulfur (S) and the final product lithium sulfide ( $Li_2S$ ) are both insulators, and the electronic conductivity is poor, so that a large amount of conductive agent must be added to the sulfur electrode; the large difference in density between S and Li<sub>2</sub>S makes the electrode undergo a huge volume change (about 80%) during the charge and discharge process, which easily leads to the collapse of the sulfur electrode structure, which leads to the degradation of the Li-S batteries performance; the lithium polysulfide produced during charge and discharge has extremely high solubility in ether electrolytes, resulting in the "shuttle effect". Especially, the "shuttle effect" of lithium polysulfide has caused problems such as poor battery cycle performance, rapid capacity decay and overcharge, which severely restricted the further development and commercial application of Li-S batteries. As a key component of Li-S batteries, electrolyte not only plays a role in transmitting lithium cation ( $Li^{\dagger}$ ) and conducting internal circuits, but also one of the main factors that determine the overall performance of the battery capacity and cycle stability. Lithium nitrate (LiNO<sub>3</sub>) has received widespread attention as an electrolyte additive for Li-S batteries, and its mechanism of action has also been studied in depth. However, this article provides a new understanding of the mechanism of LiNO<sub>3</sub> additives through deep study and new experimental schemes. In this experimental scheme, the Li metal anode recycled by electrolyte containing  $LiNO_3$  additive and fresh sulfur electrode was used to reassemble the battery with the electrolyte without the LiNO<sub>3</sub> additive; the sulfur electrode recycled by electrolyte containing LiNO<sub>3</sub> additive and fresh Li metal anod were used to reassemble the battery with the electrolyte without the LiNO<sub>3</sub> additive; both batteries have serious overcharging during the charging process, and the shuttle of polysulfide anions occurs. This shows that the mechanism of LiNO<sub>3</sub> inhibiting the "shuttle effect" is not just to form SEI film. Through the ion migration number test, it is found that after adding LiNO<sub>3</sub> additive, the migration number of Li<sup>+</sup> increases, resulting in a significant decrease in the migration of polysulfide anions. It can be concluded that another effect of adding LiNO<sub>3</sub> additives is to increase the migration number of  $Li^+$ , thereby reducing the migration number of anions and effectively inhibiting the "shuttle effect". At present, the components of gunpowder (sulfur, nitrate, carbon) are concentrated in Li-S batteries, which may be potentially dangerous during commercial use. According to the new discovery of the role of LiNO<sub>3</sub> additives in Li-S batteries in this work, future research work can be based on the migration number theory to find other electrolyte additives that can promote the migration number of lithium ions and interact with polysulfide anions. LiNO<sub>3</sub> additives, thereby reducing the potential dangers of Li-S batteries in use.

### lithium nitrate (LiNO<sub>3</sub>), lithium sulfur (Li-S) battery, lithium ion (Li<sup>+</sup>) migration number, shuttle effect

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