

废旧锂离子电池正极材料的湿法回收和再生技术研究进展

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摘 要: 随着中国新能源汽车退役高峰期的到来, 废旧锂离子电池的回收已成为一个亟需解决的问题。废弃电极中富含锂、钴、镍等金属的正极材料具有极大的经济价值, 发展高效的回收技术不仅有利于促进“双碳”目标推进, 而且能够实现固体废弃物资源化与高值化转化。在各类回收技术中, 湿法再生技术工艺成熟, 回收效率高, 是一种极具潜力的回收技术。在此, 本文综述了湿法再生技术的发展, 内容涵盖废弃正极材料的浸出、分离、提纯与再合成方法。首先, 介绍了酸/氨/深共晶溶剂浸出、生物浸出与电化学浸出等湿法再生策略以及对应策略在浸出阶段的辅助方法。随后基于浸出液的分离与提纯技术, 进一步概述了化学沉淀法、溶剂萃取法、离子交换法与膜分离法等提纯技术。针对正极材料再合成介绍了高温固相法与溶胶-凝胶法等策略。最后, 总结了湿法再生技术的瓶颈并提供可能的解决方案, 为湿法再生技术发展提供借鉴。

关键词: 废旧锂离子电池; 正极材料; 湿法; 回收; 再生

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能源驱动社会向前发展的同时也带来了能源危机、温室效应、环境污染等各种挑战。可再生能源已被用于解决这些问题, 但目前的风能、太阳能等清洁能源在能量生产过程存在间歇性, 需要依赖储能技术提供稳定的能源供给^[1]。因此, 可充电锂离子电池(LIBs)成为研究热潮, 并且是最重要的储能技术之一。随着功率密度和能量密度的不断提升, LIBs 的应用不再局限于便携式设备储能, 逐步拓展到电动汽车(EV)领域。在碳达峰、碳中和背景下, 电动汽车的应用成为减污降碳的重要途径。与同等的汽油和柴油汽车相比, 电动汽车在整个生命周期内的排放量大大减少^[2]。在一系列政策及其他因素的推动下, 电动汽车大量涌入市场。预计 2025 年 EV 的销量将达到 1100 万辆, 到 2030 年将达到 2000 万辆^[3]。然而, LIBs 的使用寿命为 5~8 年, 首批使用的电动汽车电池已经达到寿命极限, 面临退役^[4]。巨量的废弃 LIBs 中存在丰富的金属元素, 具有较高的回收经济价值与碳效益^[5]。此外, 原料储量、环

境效益和国际形势等因素给 LIBs 的原材料供应链带来巨大压力^[6]。为突破原料供应限制和顺应可持续发展的大趋势, 对 LIBs 进行回收处理, 构建生产—销售—回收—再生产的闭环资源利用路径迫在眉睫。近年来, 火法冶金、湿法再生和直接再生工艺成为废旧 LIBs 回收工艺路线的主要部分^[7]。其中, 火法冶金对复杂化学成分的正极具有普适性, 但其回收效率低下, 锂最终会变成炉渣且高温回收条件给能源和环境带来了严峻的挑战^[8]。直接再生虽然过程简化, 但 LIBs 在循环过程中锂(Li)、镍(Ni)、钴(Co)、锰(Mn)等金属元素存在不同程度的损失。从健康程度不同的电池到衰减程度不同的正极片, 再到结构变化不一的正极颗粒, 仅通过测试取样的废旧正极粉末的 ICP(电感耦合等离子体发射光谱仪)结果无法准确地将损失的金属元素补充给废旧 LIBs 正极, 导致难以精确控制不同元素之间的比例, 在大规模应用中难以处理不同降解程度的正极^[9]。湿法再生工艺通过浸出废旧正极粉末回收多种金属组分,

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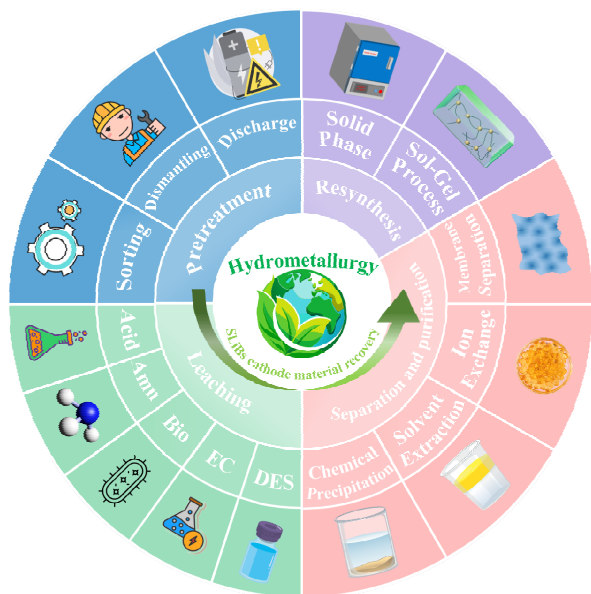
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可生产高纯度产品, 是世界上应用广泛且较为成熟的技术。

图 1 总结了湿法回收技术的发展, 涵盖正极材料的浸出、分离、提纯与再合成方法。首先总结了废旧正极的常规处理手段。随后, 对溶液浸出方式、辅助浸出手段的最新进展进行了总结, 分析了不同浸出方式随技术手段创新的演化。同时, 介绍了回收产品提纯相关的技术进展。最后, 总结了湿法再生技术的瓶颈并提供可能的解决方案。



Amn is ammonia. Bio is biology. EC is electrochemistry. DES is deep eutectic solvents.

图 1 废旧 LIBs 正极材料湿法再生技术概述

Fig. 1 Overview of hydrometallurgy regeneration of spent LIBs cathode materials

1 预处理

退役后的废旧 LIBs 在获得废旧正极粉末前需进行放电、拆解、分离等预处理操作^[10-12]。

分类后的废旧 LIBs 内仍含有残余的电量, 需进行放电处理, 预防后续的自然爆炸等安全隐患。常规的放电方式有物理放电和化学放电, 采用氯化钠盐水放电的策略最为常见^[13-14]。拆解过程中常采用物理方法将电池外壳和内部部件拆卸分离, 得到废旧正极(负载正极的铝集流体)和负极(负载负极的铜集流体)。正极材料和铝箔集流体的分离主要采用有机溶剂分离与高温分解分离法 2 种方法, 同时去除聚偏二氟乙烯(PVDF)黏结剂。N-甲基吡咯烷酮(NMP)是最常见的一类有机溶剂, Fan 等^[15]采用 NMP 溶剂有效分离了铝箔和正极活性材料, Jiang

等^[16]通过高温热解去除了 PVDF。除了黏结剂外, 循环过程中铝箔腐蚀使得铝杂质以及电解液分解产物进入正极。碱浸渍^[17-19]预沉淀策略已成功应用于去除铝(Al)等杂质金属, 干燥后筛分获得除杂正极粉体。

2 浸出

在预处理完成后的废旧正极粉料中加入浸出剂(如酸、碱等化学试剂), 可使其转化为 Li、Co、Ni、Mn 等金属离子的浸出液。为实现废旧正极的高效绿色浸出, 在浸出剂的选择上需要同时兼顾经济和环境效益。探索绿色环保、可循环利用的浸出剂是废旧 LIBs 湿法回收技术的研究热点。另外, 采用其他辅助方法协同浸出有望减少浸出剂用量, 以更加经济、更加温和的工艺实现高效、绿色浸出。

2.1 酸浸出

酸类浸出剂可分为无机酸类和有机酸类。硫酸(H_2SO_4)、盐酸(HCl)、硝酸(HNO_3)等传统的无机酸作为浸出剂时, 能够实现高效浸出, 然而三元 $\text{LiNi}_x\text{Co}_y\text{Ni}_{1-x-y}\text{O}_2$ (NCM)中的氧化物通常以高价态形式存在, 需要添加如过氧化氢(H_2O_2)、葡萄糖($\text{C}_6\text{H}_{12}\text{O}_6$)、硫代硫酸钠($\text{Na}_2\text{S}_2\text{O}_3$)等还原剂协同浸出, 如图 2a 所示^[20]。Mukai 等^[21]阐明了 H_2O_2 和 HNO_3 协同浸出 $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622)的反应机理, 通过揭示 NCM622 相的存在, H_2O_2 在其表面会发生连续的氧化和溶解反应, 从而使 NCM622 快速完全溶解。

除还原剂的协同作用外, 酸浓度和还原剂用量也决定了正极的浸出效率, 如图 2b 所示^[22]。Yu 等^[23]分析了 H_2SO_4 浓度、 H_2O_2 用量和温度对 LiCoO_2 (LCO)表面相互作用能的增强效果, 证明了 H_2O_2 用量的增强效果优于温度优于 H_2SO_4 浓度。Cerrillo-Gonzalez 等^[24]则通过在双半间歇模式下, 配合低浓度 0.1 mol/L 的 HCl 和高浓度 1 mol/L 的 H_2O_2 的还原剂能够显著提高浸出过程中金属离子的选择性, 实现了 99% 的 Li 和 96% 的 Co 提取。

尽管无机酸类浸出剂能够高效溶解废旧正极, 但在实际工业运用中会产生大量的酸性废水、废气, 对环境造成极大危害。有机酸相较于无机酸, 在同等浸出过程中, 反应体系更加温和, 对环境更加友好, 常见的有机酸如甲酸(CH_2O_2)^[25]、甘氨酸($\text{C}_2\text{H}_5\text{NO}_2$)^[26]、抗坏血酸($\text{C}_6\text{H}_8\text{O}_6$)^[27]等。Okonkwo 等^[28]以甲磺酸为浸出剂, 通过使用糖基还原剂在 $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523)中浸出大于 98% 的 Li

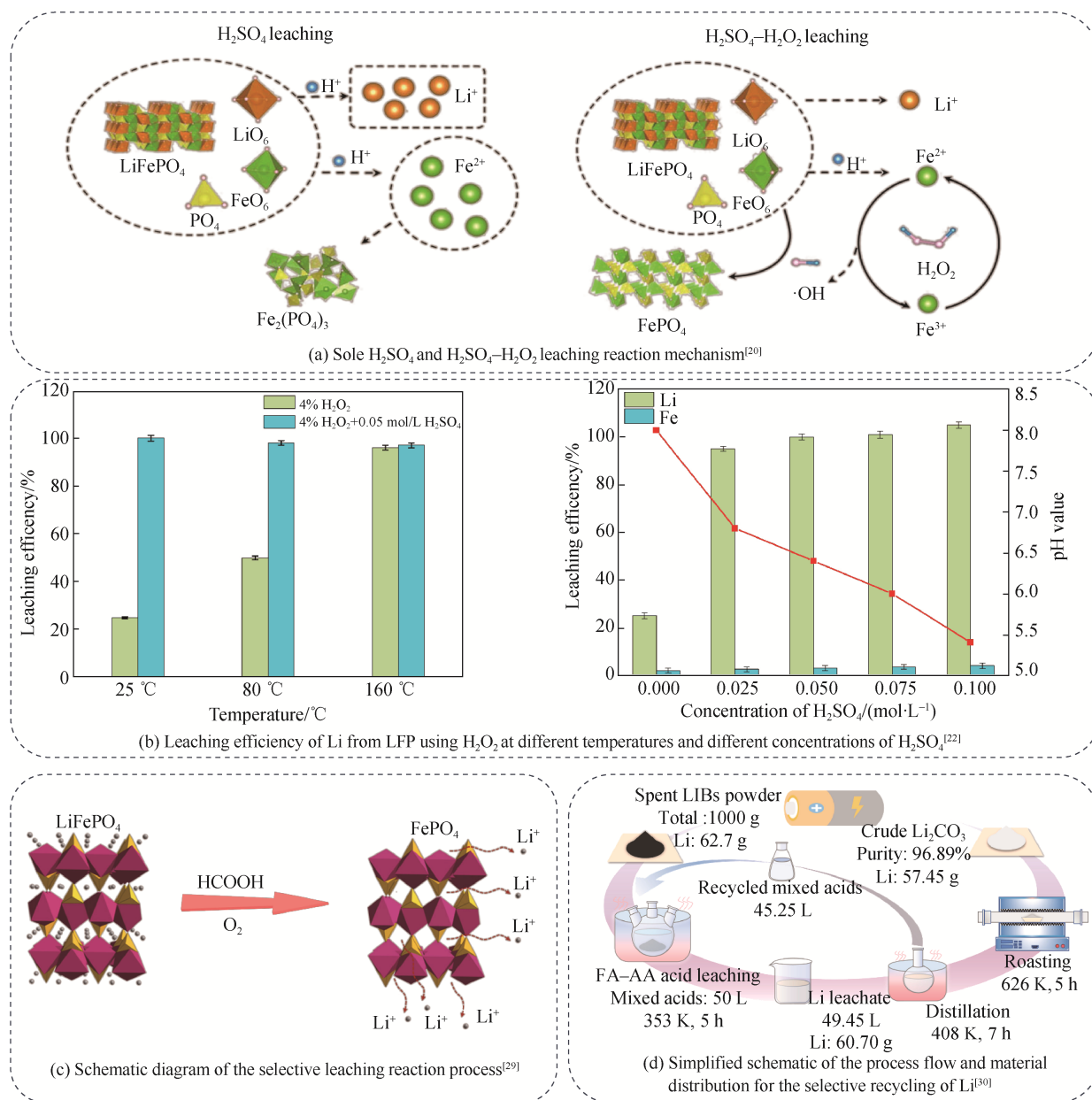


图2 废旧 LIBs 湿法回收工艺中酸浸出策略示意图

Fig. 2 Schematic diagram of acid leaching strategy in spent LIBs hydrometallurgical recovery process

与大于 88% 的 Co 和 Ni。对于 LiFePO_4 (LFP)，由于在常态状态下 Fe^{2+} 较难完全转变为 Fe^{3+} ，采取合适的氧化还原策略使得铁离子以 FePO_4 可沉淀物的形式存在，从而更好地浸出锂离子而除去杂质铁离子。因此，如图 2c 所示，Zhao 等^[29]采用环境友好的甲酸，仅用氧气和空气分别作为氧化剂和还原剂分别实现了 99.9% 和 97.81% 的 Li 浸出率。

有机酸酸性比无机酸弱，在选择性浸出上更具优势，并且有机酸可被生物降解，对环境更加友好。然而，有机酸稳定性较差，高温易分解。更弱的酸性导致其浸出用量通常高于无机酸，浸出剂成本需

要进一步考虑。

组合酸协同浸出体系的构建成为提高选择性浸出有价金属离子的突破方向之一，选取合适的组合酸可作为浸出剂和还原剂使用，减少其他试剂的使用并提高浸出效率。如图 2d 所示，Zhang 等^[30]构建了甲酸-乙酸协同浸出体系，通过调节反应条件，抑制非目标金属的浸出，选择性回收了近 96.81% 的 Li。而 Bhagaskara 等^[31]采用 $\text{H}_3\text{PO}_4\text{-H}_2\text{C}_2\text{O}_4$ 组合酸浸出 NCM，99.90% 的目标 Ni 被选择性浸出，该组合酸有望成为选择性回收 Ni 的绝佳选择之一。

2.2 氨浸出

氨浸出剂通常为 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 、 $(\text{NH}_4)_2\text{CO}_3$ 和 $(\text{NH}_4)_2\text{SO}_4$ 等溶液, NH_4^+ 与铜、镍、钴等过渡金属离子发生络合反应形成络合物, 其溶解性与稳定性形成差异, 实现选择性浸出, 这与全金属离子浸出的酸浸方法有所区别, 如图 3 所示。Yu 等^[32]通过 $\text{NH}_3 \cdot \text{H}_2\text{O}$ – $(\text{NH}_4)_2\text{CO}_3$ 浸出剂对 NCM 高效分离回收 Li、Ni、Co 和 Cu, 并通过氨蒸馏回收利用浸出液和

母液, 回收了约 93% 的 Co 和 64% 的 Li。Yang 等^[33]以水合肼为还原剂, 在氨蒸馏过程中, Ni 和 Co 的浸出率分别高达 95% 和 99%。

相较于酸浸出策略, 氨浸出的最大优势在于能够对过渡金属离子选择性浸出, 同时在后续的蒸馏过程能够回收浸出剂和母液, 大大减少了资源的浪费和废液的排放。但氨水易挥发, 刺激性强, 对工厂防护和设备要求较高。

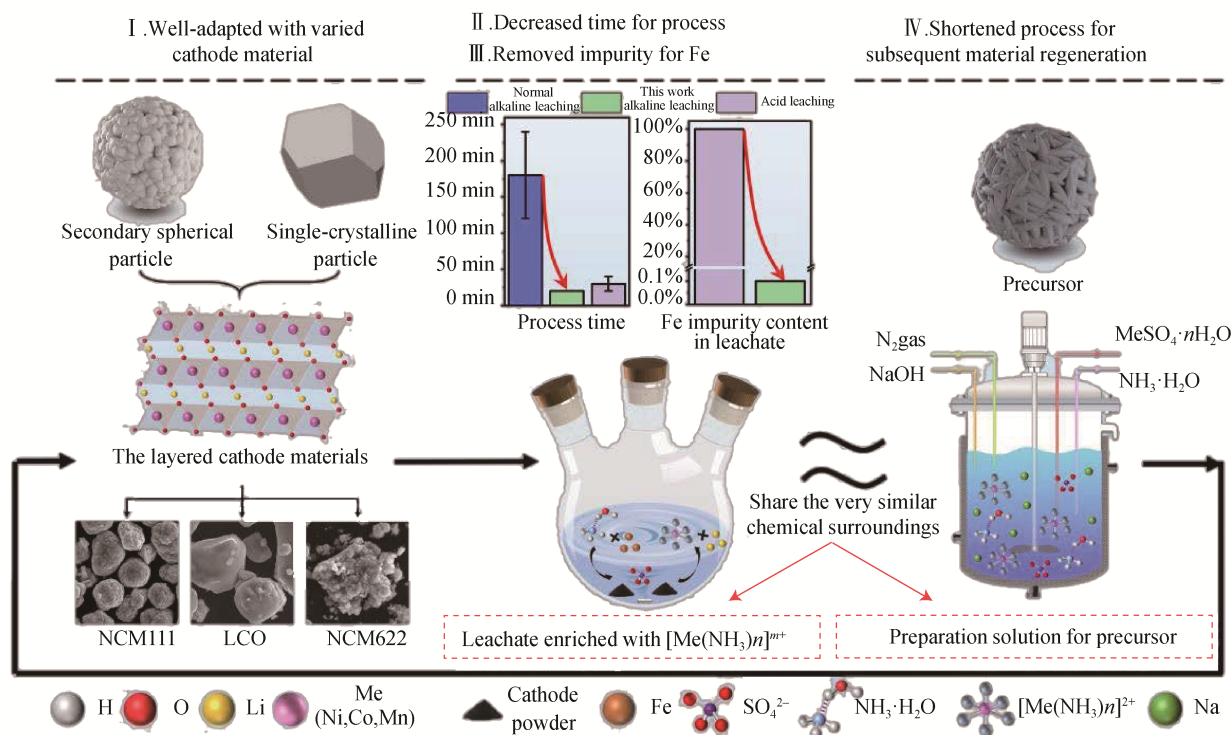


图 3 碱性浸出在废旧正极材料回收中的优势^[34]

Fig. 3 Advantages of alkaline-leaching in the recycling of spent cathode materials^[34]

2.3 生物浸出

生物浸出是利用在生命活动中具有产酸和自身氧化/还原特性的微生物实现对正极材料的溶解, 使其成为离子态存在于浸出液中, 便于后续的分离和提取, 从而实现有价金属的回收。常用的微生物如氧化亚铁硫杆菌、氧化硫硫杆菌等。Yun 等^[35]对矿山中分离得到的 5 株菌株(N10、P6、P7、N4 和 F-O5)与氧化亚铁硫杆菌分别对 NCM111、NCM523 和 NCM622 进行浸出, 实验证明 N10 和 P7 菌株对 NCM111 中 Li、Ni、Co、Mn 的浸出率高达 95%, 但对于 NCM523 和 NCM622 的金属浸出率较低。同时还验证了浸出液中 Ni 浓度过高对细菌活性有负面影响。Yang 等^[36]调查了废旧 LCO 正极电池中金属的生物浸出, 利用不同微生物的适应联合体对比

浸出效果, 结果表明粒度和微生物菌群适应性也能显著影响金属回收效率。另外, Naseri 等^[37]利用氧化硫硫杆菌自身产酸的性质, 相较于直接生物浸出, 以生物源硫酸作为浸出剂的间接生物浸出使得 Li 和 Mn 的浸出率分别为 93% 和 53%。

与传统的酸浸出工艺相比, 绿色、环保、无污染是生物浸出的最大优势, 其低廉的成本优势在未来具有较大的潜力。但由于微生物的培养环境较为苛刻, pH 值、温度等均会影响浸出效果。特别在金属离子浓度较高的溶液中, 大部分微生物难以繁殖和生存, 商业化应用仍充满诸多挑战。

2.4 深共晶溶剂浸出

如图 4a 所示, 深共晶溶剂(DES)是由 2 种或 3 种化合物通过氢键作用合成的一类低熔点共晶混

合物, 具有生物可降解、制备简单、来源广泛、可回收利用、高溶解金属氧化物等优点。DES 具有还原性, 因此其本身既可作为浸出剂也能作为还原剂使用。如图 4b 所示, 在浸出过程中, DES 渗透进正极材料内部, 溶解其中的有效成分, 随后这些成分扩散到溶剂中, 形成浸出液。Lou 等^[38]混合草酸、氯化胆碱、乙二醇合成的 DES 浸出剂, 在最佳条件下, NCM111 浸出率超过 96%, 且渗滤液可回收利用。

Wang 等^[39]通过柠檬酸和氯化胆碱制备了 DES 浸出剂, 对 LiNiO_2 (LNO) 的浸出率可达到 94.51%, 对于 NCM、LCO 正极材料, 该策略也具有普适性。

虽然 DES 的提取效率高, 但在某些情况下其选择性可能不如传统浸出剂, 另外 DES 的稳定性仍受到 pH 值、温度等影响, 同时研发和生产可能涉及较高的成本, 这会影响其在市场上的普及和应用。

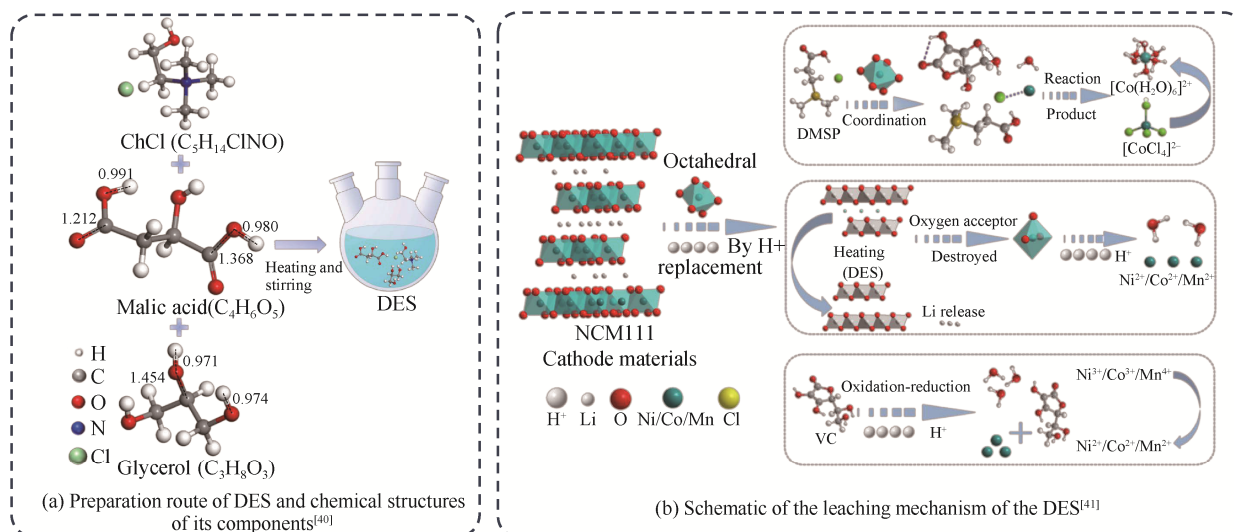


图 4 DES 的制备和浸出机理示意图

Fig. 4 Schematic diagram of preparation and leaching mechanism of DES

2.5 电化学浸出

图 5a 展示了电化学法在浸出正极方面的应用。电化学浸出是一种利用电化学方法从固体材料中提取锂的技术, 所依赖的电解质常为硫酸钾(K_2SO_4)、碳酸钠(Na_2CO_3)、氯化钠(NaCl)等溶液。图 5b 分析了电化学法浸出 NCM 正极材料机理, 通过在浸出过程中施加电压, 促使 Li^+ 从正极材料中溶出进入电解质溶液。Yang 等^[42]使用 K_2SO_4 溶液, 将 NCM622 正极材料作为阳极和同尺寸的铜阴极直接电化学浸出 Li^+ , 实现了近 100% 的 Li 浸出率。而 Chen 等^[43]把废旧 NCM 正极粉末制备的电极片作为阳极, 相同尺寸的钛片作为阴极, 在 Na_2CO_3 溶液中施加电压, 最佳条件下 Li^+ 的浸出率可达 85.20%, 锂的选择性接近 100%。

另外, Tian 等^[44]建立了一种间接电化学浸出策略, 即在 Na_2SO_4 电解质溶液下以高析氧电位的掺硼金刚石电极为阳极, RuO_2/Ti 为阴极, 生成氧化物种, 增强氧化反应接触的间接氧化 LFP 的电化学体系, Li^+ 的浸出率达 95.53%, 铁离子的浸出率小于 0.01%。

尽管电化学浸出技术可以减少碳排放和现场污染释放, 对环境更加友好, 并对有价金属的回收更加高效。但如图 5c 所示, 在实际大规模处理应用中相较于酸浸策略而言存在一些不足。例如, 有待开发相关的大型设备, 操作成本可能较高, 对于各类有价金属精确回收的操作条件也更为复杂等。

2.6 辅助浸出方法的应用

除了选择合适的绿色试剂和浸出形式提高浸出效率实现减污降耗, 还可采取辅助措施, 在原有浸出策略上减少浸出剂用量、提升选择性浸出效率等。

2.6.1 机械活化 机械活化通常采用机械力作用于颗粒, 使颗粒细化, 增加其表面缺陷并促进极性分子或离子进入内部空穴, 增强反应活性, Chen 等^[45]则将废旧 LIBs 与天然有机还原剂荔枝皮粉(LPP)和柠檬酸进行共球磨浸出, 通过物理作用破坏正极材料的晶体结构, 加速晶格畸变, LPP 在柠檬酸作用下加速金属氧化物溶解, Li、Co、Mn 和 Ni 的浸出率分别为 99.21%、96.52%、98.21%和 94.79%。与常规有机酸浸出相比, 有机酸用量减少约 86.67%。

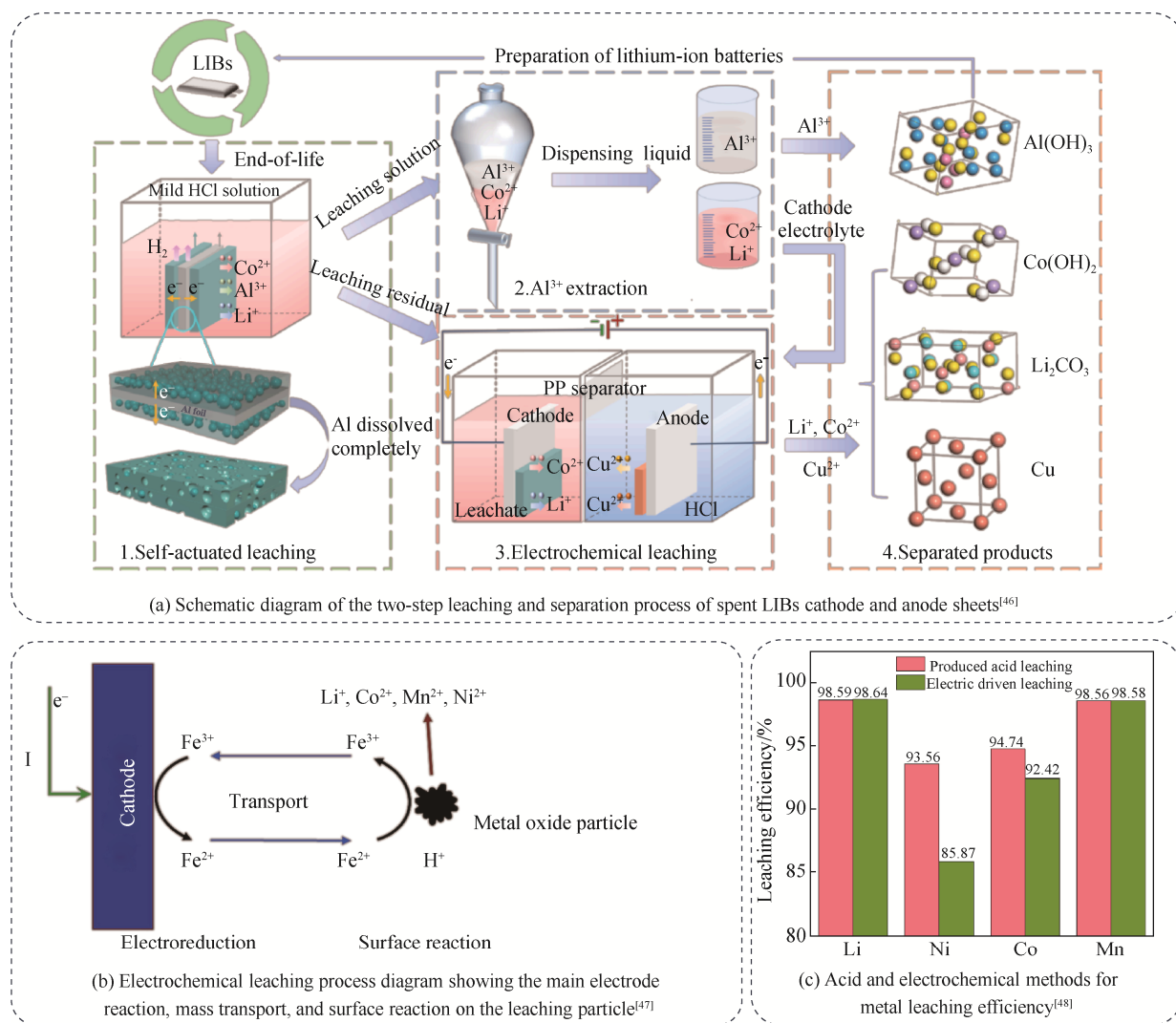


图 5 废旧 LIBs 湿法回收工艺中电化学浸出策略示意图

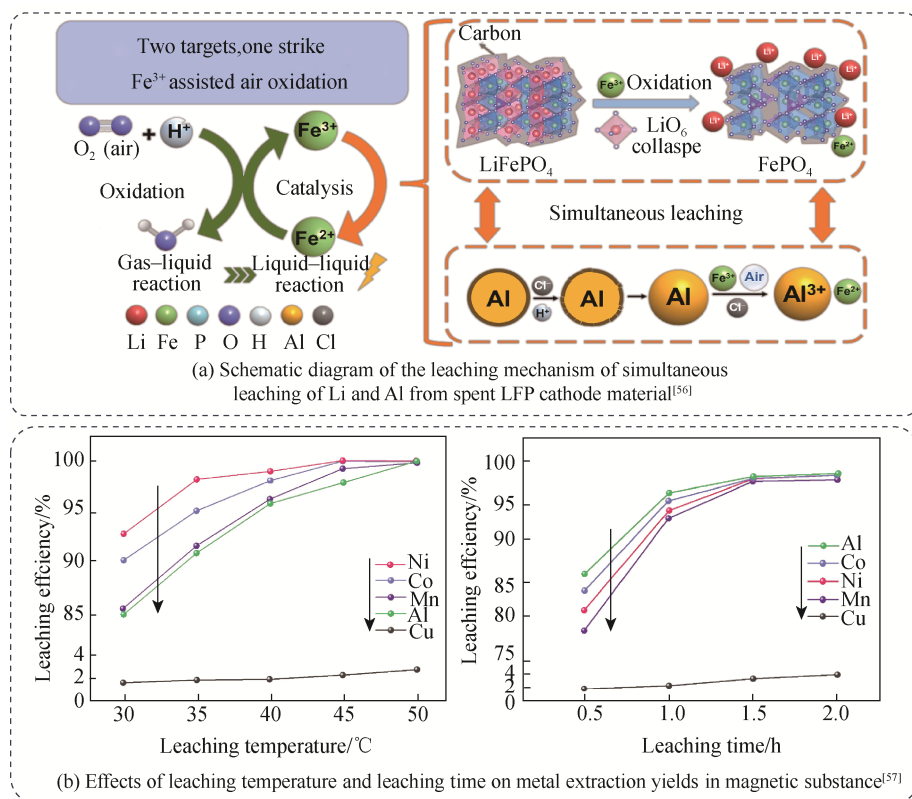
Fig. 5 Schematic diagram of electrochemical leaching strategy in spent LIBs hydrometallurgical recovery process

2.6.2 $\text{Fe}^{3+}/\text{Fe}^{2+}$ 氧化还原介质 由图 6a 可见, 对于 LFP 正极材料, Fe 离子的引入有利于提高前驱体 FePO_4 纯度, 同时可重复利用, 并不会额外产生其他杂质金属离子。Niu 等^[49]以 $\text{Fe}_2(\text{SO}_4)_3$ 为浸出剂, Li^+ 浸出率为 99.41%, FePO_4 回收率为 96%。

对于 Fe 离子的来源, 除了常规的含铁化学试剂, 在矿物中也可以获取 Fe 离子, Liu 等^[50]以黄铁矿(FeS_2)和元素 S 的联合使用, 在生物浸出阶段提高了铁-硫氧化菌的活性, 增强其产酸能力, 这有效地促进了高价金属氧化物的还原, Li、Ni、Co、Mn 的浸出率均接近 100%。正如图 6b 所示, 磁性 Fe 离子同样能够有效提高浸出效率。Borra 等^[51]在稀土元素基(NdFeB)磁体用 H_2SO_4 浸出得到废 FeSO_4 溶液用于还原浸出正极材料。在此过程中, 稀土元素、Li、Ni、Co 和 Mn 的总回收率超过 95%。Kim 等^[52]利用磁性 Fe^{2+} 氧化嗜酸氧化

亚铁硫杆菌并产生细胞内磁性纳米粒子, 实现近 100% 的 Li 浸出率。

2.6.3 波动辅助 波动辅助可分为机械波辅助和电磁波辅助, 以能量传递的波动促进浸出。机械波辅助通常采用超声波, 可增强混合物中金属氧化物的溶解^[53]。Okonkwo 等^[54]将糖蜜、甲烷磺酸和超声波联用, 与传统机械搅拌相比, 超声波与浸出液相互作用形成的空化气泡导致正极材料颗粒破碎, 使得反应物和形成产物的传质速率提高, 可浸出 97% 的 Li 和 Ni、95% 的 Co 以及 91% 的 Mn。而 Li 等^[55]利用接触带电产生的自由基来促进超声波下的金属浸出, 对于 LCO 正极, Li 的浸出效率可达到 100%, Co 的浸出效率达到 92.19%。对于 NCM 正极, Li、Ni、Mn 和 Co 的浸出率可分别达到 94.56%、96.62%、96.54%、98.39%。

图6 $\text{Fe}^{3+}/\text{Fe}^{2+}$ 氧化还原介质对废旧LIBs湿法回收工艺的辅助示意图Fig. 6 Auxiliary schematic diagram of $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox medium for hydrometallurgical recovery process of spent LIBs

微波作为一种电磁波，在浸出过程中其释放的能量可被正极材料吸收，提高其内部温度使其分子振动加剧，加速了溶剂的穿透力。Li等^[58]用微波辅助柠檬酸- H_2O_2 浸出体系，柠檬酸除了具有还原能力外，在微波辅助浸出过程中还能与Cu和Fe螯合形成还原自由基，提高金属浸出率，最佳条件下可浸出99.5%的Li和Co、99.3%的Ni以及99.7%的Fe。

2.6.4 其他 此外，讨论了其他辅助方法，通过氧化法强化浸出过程中，Kang等^[59]提出了一种超临界水氧化法辅助NCM333的酸浸出策略，Ni、Co、Mn的浸出率分别高达99.7%、96.8%、98.5%。并讨论了超临界水氧化过程中的形态变化和元素的迁移机理对于PVDF的有效分解以及 H_2O_2 用量影响。Liu等^[60]利用 $\text{Ca}(\text{ClO})_2$ 强氧化特性，可在LFP正极材料酸浸阶段中提供氧化剂和净化剂作用，能够同时实现目标组分 Li^+ 、 Fe^{3+} 和 Ca^{2+} 杂质的分离富集，这是机械活化所不具有的优势。另外对于LFP正极材料，可用 $\text{Na}_2\text{S}_2\text{O}_8$ 氧化强化浸出剂回收 FePO_4 ^[61]，并通过氧化石墨烯进行涂覆制备电化学性能更加优越的正极材料，如钠离子电池正极材料^[62–63]。

生物浸出法普遍采用直接生物浸出策略，但浸出效果欠佳，因此Tian等^[64]利用腐殖酸驯化菌株对

NCM正极材料进行浸出，与未驯化菌株相比，Li、Ni、Co和Mn的浸出率分别从90.69%、55.53%、40%和50%提高至100%、85.06%、74.25%和69.44%。

3 浸出液的分离和提纯

由于浸出液中含不同金属离子，因此需要通过分离和提纯使Li、Co、Ni、Fe等离子以金属盐或含氧酸盐的形式进行回收，如 Li_2CO_3 、 CoC_2O_4 、 NiSO_4 、 FePO_4 等产物，提纯后作为产品或用于再次合成正极材料。

3.1 化学沉淀法

化学沉淀法是通过向金属离子溶液中加入沉淀剂获得对应金属盐。对于单一金属阳离子的回收，例如LCO正极材料，通常采用草酸作为沉淀剂^[65–67]。 Co^{2+} 在一定条件下与草酸反应生成 CoC_2O_4 沉淀，干燥后可用于合成LCO正极材料。含 Li^+ 滤液加入 Na_2CO_3 获得 Li_2CO_3 沉淀^[68–70]。

而共沉淀法则通过加入沉淀剂得到含2种及以上金属元素的金属盐沉淀，可提纯得到正极材料的前驱体，一般多用于富含多金属离子的NCM浸出液。Su等^[71]采用分级沉淀的策略，使用

$\text{NH}_3 \cdot \text{H}_2\text{O}$ - NaOH 调节 pH 值分别沉淀 Fe 和 Ni/Co/Mn 共沉物。

与电化学浸出溶解有价金属的策略不同, 电沉积法是在外加电流控制下, 金属离子在电解质溶液中通过电极反应被还原为金属并沉积在电极表面的过程。Pei 等^[72]采用电解 CuSO_4 制 H_2SO_4

实现高效浸出和沉积, 可回收得到 Ni-Co 合金、 MnO_2 、 Li_2CO_3 和 Cu 单质。如图 7 所示, Yao 等^[73]以废 LiMn_2O_4 (LMO)为原料, 通过电沉积策略将锂离子与铵离子引入到 MnO_2 中, 得到具有碳布基底的氧化锰薄膜($\text{LNMO}_d@\text{CC}$), 作为水性锌离子电池的新型正极材料, 表现出优异的电化学性能。

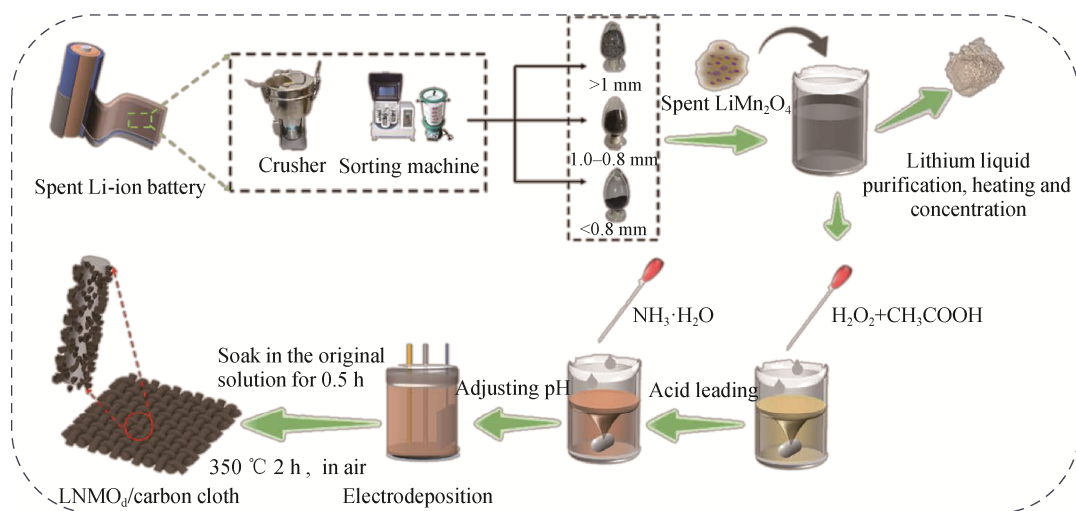


图 7 $\text{LNMO}_d@\text{CC}$ 复合材料的示意性合成^[73]

Fig. 7 Schematic synthesis of the $\text{LNMO}_d@\text{CC}$ composite^[73]

3.2 溶剂萃取

溶剂萃取法是一种常用的分离技术, 利用相似相溶的原理使目标金属离子选择性地从水相转移到有机相中形成金属螯合物, 从而实现有价金属离子的选择性分离。常见的萃取剂包括 P204、P507、Cyanex272 等^[74]。合理地选取混合萃取体系能够提高其萃取分离的效率, Qing 等^[75]将 D2EHPA 与 TBP 萃取剂结合实现了 99.9%以上的 Fe 和 Al 杂质的深度去除, 而 Han 等^[76]通过将 HEH(EH)P 与 Cyanex301 萃取剂结合发现, 该混合萃取剂对 Ni^{2+} 有很强的协同萃取作用, 实现了 Ni^{2+} 、 Co^{2+} 、 Mn^{2+} 的协同萃取。

离子液体(IL)作为一类新型的绿色萃取剂, 具有高度选择性和再生性, 相关研究表明 IL 与盐类组成双水相体系(ABS)可有效提高萃取效率。Li 等^[77]将三丁基十四烷基氯化磷(P_{44414})Cl 和 NaCl 组成 ABS, 有效分离了 LFP 中的 Fe 与 Li。Mušović 等^[78]将四丁基磷离子液体(ILS)和硫酸铵组成 ABS, 提高了 Co^{2+} 与 Li^+ 的选择性分离, 同样证明了双水相体系在离子分离方面的有效性。

溶剂萃取法的最大特点是能够实现高选择性分离, 操作过程简单, 易于实现自动化, 不需要复杂的仪器设备, 但萃取剂大多为有机溶剂, 具有一定

的毒性, 可能对人体健康和环境造成威胁, 随着对环境保护要求的提高, 研究和开发更绿色、更安全的萃取技术仍然是重要的研究方向。

3.3 离子交换

离子交换(IX)是一种基于离子交换树脂或离子交换聚合物的工作原理的分离技术, 其中离子交换树脂是一种多孔高分子化合物, 化学结构独特, 可以通过吸附和释放溶液中的离子来进行离子交换。Gong 等^[79]使用氢型强酸性阳离子交换树脂(HR), 通过离子交换有效地吸附了浸出液中的 Ni、Co、Mn 和 Li 离子, 降低了成本, 实现了化学性质相似的金属离子的分离。此外, 基于树脂的珠粒尺寸设计的 IX 多塔配置能够连续生产高纯度(>99.5%)的含 Li、Ni 和 Co 的萃余液^[80]。Lei 等^[81]采用顺序共沉淀与离子交换树脂吸附结合的策略, 在 NCM 浸出液中通过 NaOH 实现了 Al、Fe、Cu 杂质金属的分离, 而离子交换树脂具有良好的吸附分离作用, 分别得到富 Ni/Co/Mn 和富 Li 渗滤液, 可分别生成 NCM 前驱体与 Li_2CO_3 。

沸石作为分子筛的代表性材料, 在离子交换作用上具有优越的性能。Huo 等^[82]通过 NaA 沸石离子交换, 实现了浸出液中 Li、Mn、Ni、Co 等金属离

子的有效分离, 确定离子交换选择性顺序为 $\text{Mn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Li}^+$ 。

离子交换树脂/聚合物可以反复再生使用, 长期运行成本较低, 但其普遍适用性较差, 当溶液中的离子种类较多时, 需要针对不同目标离子选择不同材料, 这将增加体系复杂性和成本。

3.4 膜分离

膜分离技术是一种以分离膜为核心进行分离、浓缩和提纯物质的一门新兴技术, 如图 8 所示^[83]。径迹蚀刻膜是一种微滤膜(MF), Troitskiy 等^[84]使用带正电荷的聚二甲基烯丙基氯化铵对径迹蚀刻膜进行改性, 以增加对双电荷离子的排斥, 从而更有

效地选择性分离 Li。而孔径更小的纳滤膜(NF)可更好地允许单价离子(如 Li^+)通过, 高效截留二价及多价金属离子(如 Ni^{2+} , Co^{2+} 和 Mn^{2+})。另外, He 等^[85]提出了一种基于带正电的纳米级分散夹层的聚酰胺纳滤膜(TFC-NF), 首次应用于从废旧三元 LIBs 浸出液中回收 Li。夹层内的正电荷削弱了电负性, 增强了 Donnan 排斥效应, 实现了浸出液中 Li^+ 的高纯度(分离因子 ≥ 93.5)和高回收率(79.2%), 优于大多数 NF 膜。Foo 等^[86]在 TFC-NF 膜上涂有富含铵基的聚电解质, 利用铵基在低 pH 值下形成静电屏障, 选择性地阻碍多价阳离子传输。对于 NCM 浸出液, 该涂层膜可实现超过 99.5% 的渗透液 Li 纯度。

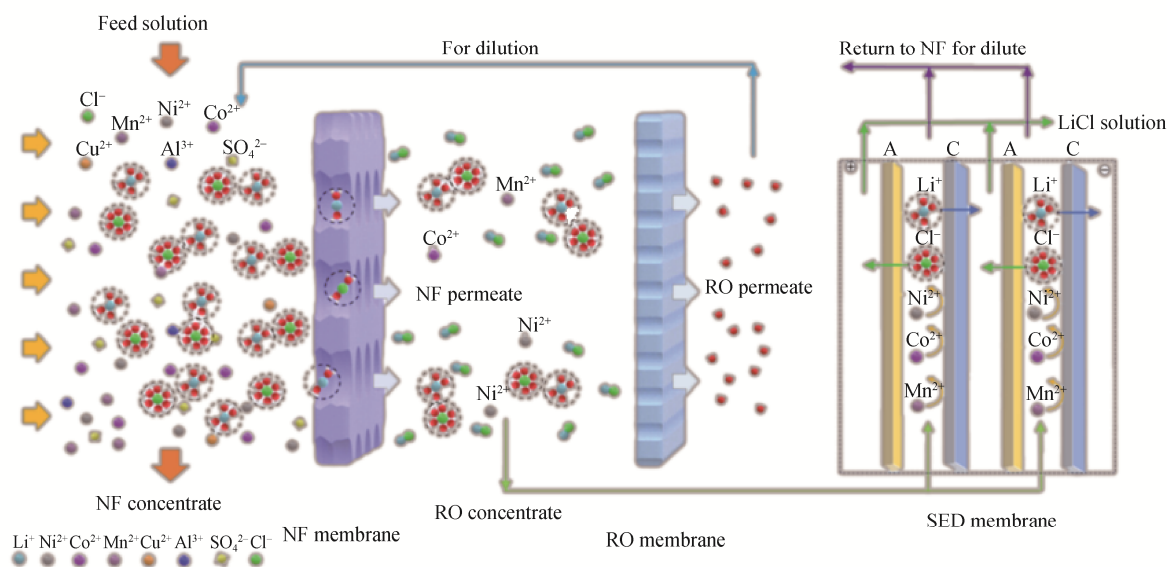


图 8 多级膜耦合分离富集锂示意图^[83]

Fig. 8 Schematic diagram of multistage membrane coupling separation and enrichment lithium^[83]

印迹膜是分子印迹技术与膜分离技术耦合的一类具有分子尺度选择性的分离膜, 具有对模板的“记忆”空穴, 即目标分子的形状以及与目标分子中功能基团相互作用的排列, 被储存在膜材料中。Qu 等^[87]通过环保水解聚合合成了 TiO_2/PVDF 基锂离子印迹膜(LiIMs), 通过 Li^+ 与冠醚上的氧在表面活性吸附位点的配位来实现选择性吸附。另外, 双极膜是一种特种离子交换膜, 在电流作用下实现阴阳两极膜的离子交换, Zhu 等^[88]利用双极膜电渗析从富含 Li_2SO_4 浸出液中回收 LiOH 和 H_2SO_4 。

尽管膜分离技术在浸出液中高效选择性分离 Li 具有一定优势, 但膜材料寿命较短, 需要定期更换, 且膜的透过流量和分离效果受到压力、温度、pH 值等因素的影响, 这需要严格控制操作条件, 使得运

行和维护的成本增加。

4 正极材料再生

经分离、提纯和沉淀得到金属盐前驱体和 Li 盐可经过高温固相法、溶胶-凝胶法等方法再次合成正极材料, 从而实现废旧 LIBs 材料的闭环再生。

4.1 高温固相法

高温固相法(solid phase method)通常以煅烧的方式将 Li_2CO_3 ^[89]、 LiOH ^[90]等 Li 盐与正极前驱体进行充分混合后反应再合成正极材料。特别地, Kim 等^[91]将 NCM 浸出液中分离的富 Mn 浸出渣添加 Li、Al 源烧结后, 再合成了新型三元 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)正极材料。

对于新型正极材料的再合成, Zhang 等^[92]将

浸出分离得到的 $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) 前驱体以 $\text{Ni}:\text{Fe}:\text{Mn}=1:1:1$ 的摩尔比混合, 并加入 Na_2CO_3 高温焙烧再生得到新的钠离子电池正极材料 ($\text{O}_3\text{-NaNFM}$)。由图 9 可以看到, 对于 LFP 正极材

料的再合成, 需要额外引入 C 源促进 Fe^{3+} 还原为 Fe^{2+} [93]。因此, 经湿法浸出分离提纯得到的 LFP 前驱体在添加 Li 源与 C 源经高温再合成得到的 LFP/C 正极材料, 其电化学性能更具优越性[94]。

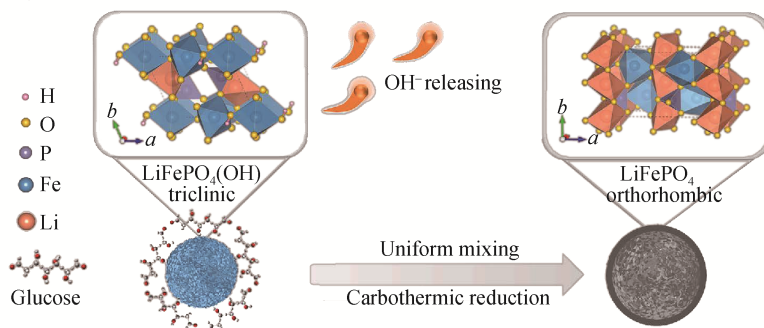


图 9 LFPOH 通过在 600 °C 用 10%(质量分数)葡萄糖进行碳热还原 5 h 转化为 LFP 的示意图[93]

Fig. 9 Schematic of phase transformation of LFPOH into LFP through carbothermic reduction at 600 °C for 5 h with 10% (in mass) glucose[93]

4.2 溶胶-凝胶法

溶胶-凝胶法通常以有机酸作为螯合剂, 促使浸出液中各金属离子均匀分散在水溶液中, 随后的水蒸发形成稳定的透明溶胶前体以溶解金属离子, 溶胶经陈化胶粒间缓慢聚合形成三维网络结构的凝胶, 通过煅烧以分解有机物并诱导结晶制备纳米级别正极材料。与共沉淀具有相似的原理, 其最大的特点在于有机酸浸出液中的 Li^+ 可不经分离提取就能直接做 Li 源进行再合成正极材料。

柠檬酸是一种良好的浸出剂兼螯合剂使用的有机酸[95], Wang 等[96]利用柠檬酸浸出后的渗滤液采用溶胶-凝胶法成功地合成了尖晶石 LMO 正极。而 Yu 等[97]采用柠檬酸溶于乙二醇制备的溶液(CAEG)同时作为浸出剂与螯合剂, 金属柠檬酸盐和乙二醇之间的酯化反应导致形成 Co 复合物, 而高温能够加速 Co 复合物的形成和生长, 相较于传统的溶胶-凝胶方法, CAEG 通过游离柠檬酸和乙二醇之间的酯化反应, 有助于形成高黏度的类似塑料的凝胶, 同时 CAEG 也适用于 NCM 正极的再生。

5 效益分析

废旧 LIBs 的回收在实际应用中, 传统的酸浸出工艺是一种常用的策略。如表 1 所示, 有效去除杂质是提高回收利润的方式之一, 可在预处理过程中进行相关除杂操作, 例如对 1t 废旧 NCM 型电池采用碱溶解处理的方式使得废旧 LIBs 中的

Al 等杂质金属去除, 在无氧条件下热处理可促进有价金属由高价态还原为低价态, 减少额外的添加剂和还原剂的使用, 提取得到的各类正极材料前驱体可获得 1891.71\$ 的利润, 同时也可通过空气烧去除其中的 PVDF 等有机杂质。在浸出条件的选取方面, 需要特别关注浸出温度、浸出时间以及浆料比(S/L)等对产品纯度、提取具有重要影响的条件。传统酸浸工艺用到的浸出剂常为 H_2SO_4 等无机酸, 考虑采用对环境友好、具有浸出剂与还原剂双重作用的有机酸也能获得相对可观的利润。

废旧 LIBs 经过浸出阶段与分离提纯阶段之后, 可得到相关电极材料的前驱体, 通过高温固相法与溶胶-凝胶法再次合成 LIBs 正极材料, 使其具有优于原始正极材料的性能并与商业化正极材料性能接近。由表 2 可知, 对于原始废旧正极材料, 由于随着循环次数的增加, 电池内部会逐渐出现极化反应, 使得部分脱离 Li^+ 不能重新嵌入, 导致不可逆容量的损失。而经过再生之后, 如 2.8~4.3 V 的电压窗口下, 再生后的 NCM523 型正极材料 (R-NCM523) 在 1C 下首次充电和放电时的比容量可达到 150.2 mA·h/g (相较于废旧 NCM523 的 113.2 mA·h/g), 经 300 次循环后容量保持率达到 75.4%, 优于废旧 NCM523 型正极材料的 54.7%。而在 2.7~4.3 V 的电压窗口下, R-NCM622 在 1C 下首次充电和放电时的比容量可达到 163.5 mA·h/g (相较于商业 NCM622 的 151.7 mA·h/g), 经 300 次循

环后容量保持率达到 85.08%，接近商业 NCM622 型正极材料的 84.67%，显示了 R-NCM622 具有良好的循环稳定性，这是由于再生后的正极材料不仅通过 Li 源的补充修复其晶体结构，同时在表面上形成新的固态电解质界面膜，使其 Li⁺得以重新进行脱嵌，延长 LIBs 的循环寿命。

表 1 回收 1 t 废旧 LIBs 的湿法浸出工艺参数及效益

Table 1 Process parameters and economic benefits of hydrometallurgical leaching for recycling 1 t of spent LIBs						
Recyclable materials	Pretreatment	Optimal conditions for leaching	Leaching efficiency	Product	Profit/\$	Ref.
NCM	Alkaline dissolution treatment followed by calcination at 600 °C for 4 h under an anoxic environment	Temperature: 95 °C, Reagent: 2 mol/L H ₂ SO ₄ , Time: 240 min, S/L of 100 g/L	Li: 100% Mn: 98.13% Co: 97.27% Ni: 97.37%	Li ₂ CO ₃ MnO ₂ CoSO ₄ NiSO ₄	1891.71	[98]
NCM	Calcination of air at 350 °C for 30 min	Temperature: 80 °C, Reagent: 0.5 mol/L C ₂ H ₂ O ₄ , Time: 20 min, S/L of 20 g/L	Li: 95.7%	Li ₂ CO ₃ (high purity)	2160.60	[12]
LCO	Calcination of air at 550 °C for 60 min	Temperature: 75 °C, Reagent: 2 mol/L NH ₂ CH ₂ COOH, 6 % (in volume) H ₂ O ₂ , Time: 100 min, S/L of 1 : 15	Li: 94.0%	Cathode precursor	2394.56	[28]

NCM is LiNi_{1/3}Co_{1/3}Ni_{1-x-y}O₂. LCO is LiCoO₂.

与 LFP 正极材料相比，富含贵金属的 NCM 正极材料具有更高的回收经济效益^[99]。在设备、试剂、能耗等成本上要求更高，不仅需要在预处理阶段进行有效的除杂操作(如碱溶解、空气煅烧和无氧热还原)以提高产品的纯度，同时采用合适的浸出策略来减少额外试剂的使用。目前传统的无机酸浸出策略仍然处于首要地位，相较于绿色环保的有机酸，无机酸(如 H₂SO₄)在批量处理上仍具备成本优势。

在 LIBs 正极材料的再合成上，高温固相法具备操作简单、反应周期短的优势，更适合工业化，但合成的材料粒度并不均一，在能耗上具有局限性。而溶胶-凝胶法在低温下进行，能耗较低，同时合成的 LIBs 正极材料成分和结构更为均匀，但反应周期

较长、使用的有机溶剂用量更大，以回收 1 t 废旧 NCM 型 LIBs 为例，溶胶-凝胶法(8361 \$)与高温固相法(6332 \$)对比，在工业化进程中成本上仍不具备优势。因此，对于溶胶-凝胶法在未来的优化，选择合适的有机溶剂来减少反应周期与用量，尽可能降低回收成本以带来更为可观的利润。而较为成熟的高温固相法可在反应温度和时间上进行突破，减少能耗所带来的成本负担。

同时如何精准、快速了解废旧 LIBs 的残余健康状态也是有效回收的重要前提^[100–102]，因此采用人工智能的机器学习方式能够快速检索市场上不同类型 LIBs 的各类数据，针对退役后的废旧 LIBs 的内部状态能够进行快速检测，实现回收的快速与准确。

表 2 回收 1 吨废旧 LIBs 的湿法再生工艺参数及效益

Table 2 Process parameters and economic benefits of hydrometallurgical recycling for 1 t of spent LIBs									
Recycled cathode	Pretreatment	Optimal conditions for leaching	Leaching efficiency	Cost/\$	Regeneration method	Original performance	Regeneration performance	Commercial performance	Ref.
R-NCM622	Calcination of	Temperature: 50 °C,	Li: 94.47%	7547	High-temperature solid-state method	No	2.7–4.3 V	2.7–4.3 V	[103]
	air at 600 °C	Reagent: 1 mol/L	Mn: 99.36%				163.5 mA·h/g	151.7 mA·h/g	
	for 5 h,	H ₂ SO ₄ ,	Co: 99.28%				at 1 C, 85.08%	at 1 C, 84.67%	
	followed by an	Time: 30 min,	Ni: 99.56%				retention after	retention after	
	additional 1 h	S/L of 60 g/L	300 cycles				300 cycles		
	of calcination								
	under an anoxic								
	environment								

(Continued Table 2)

Recycled cathode	Pretreatment	Optimal conditions for leaching	Leaching efficiency	Cost/\$	Regeneration method	Original performance	Regeneration performance	Commercial performance	Ref.
R-NCM622	Calcination of air at 500 °C for 40 min	Temperature: 90 °C, Reagent: 2.5 mol/L H ₂ SO ₄ , 1% (in volume) H ₂ O ₂ , Time: 150 min, S/L of 1 : 9	All >99%	8548	High-temperature solid-state method	No	2.7–4.2 V 138.0 mA·h/g at 1 C, 90% retention after 100 cycles	Near	[104]
R-NCM622	Calcination of air at 700 °C for 5 h	Temperature: 50 °C, Reagent: 0.5 mol/L H ₂ C ₂ O ₄ , Time: 60 min, S/L of 20 g/L	All >99%	7778	High-temperature solid-state method	No	2.7–4.3 V 152.2 mA·h/g at 1 C, 87.7% retention after 150 cycles	Near	[105]
R-NCM523	Alkaline dissolution treatment followed by calcination in air at 600 °C for 5 h	Temperature: 60 °C, Reagent: 0.47 mol/L H ₂ SO ₄ , 2% H ₂ O ₂ , Time: 30 min, S/L of 20 g/L	All >99%	8075	High-temperature solid-state method	No	2.7–4.3 V 143.5 mA·h/g at 1 C, 87% retention after 100 cycles	2.7–4.3 V 133.4 mA·h/g at 1 C, 80% retention after 100 cycles	[106]
R-NCM523	An anoxic calcination process conducted at 650 °C for a duration of 1 h	Temperature: 50 °C, Reagent: 2 mol/L H ₂ SO ₄ , Time: 90 min, L/S of 10 mL/g	All >99%	6332	High-temperature solid-state method	No	3.0–4.4 V 173.9 mA·h/g at 0.5 C, 91.9% retention after 100 cycles	Near	[54]
R-LFP	An anoxic calcination process conducted at 500 °C for a duration of 2 h	Temperature: 25 °C, Reagent: 0.6% (in volume) (H ₂ O ₂ /CH ₃ COOH), Time: 15 min, S/L of 80 g/L	Li: 99.02%	2034	High-temperature solid-state method	2.0–4.5 V 115.5 mA·h/g at 1 C, 30.0 % retention after 200 cycles	2.0–4.5 V 135.6 mA·h/g at 1 C, 98.6 % retention after 200 cycles	No	[107]
R-NCM523	Alkaline dissolution treatment followed by calcination under anaerobic conditions at 80 °C for 24 h, and subsequent calcination in air at 700 °C for 5 h	Temperature: 90 °C, Reagent: 0.5 mol/L C ₆ H ₈ O ₇ , 1.5% (in volume) H ₂ O ₂ , Time: 60 min, S/L of 20 g/L	All >95%	8361	Sol-gel method	2.8–4.3 V 113.2 mA·h/g at 1 C, 54.7% retention after 300 cycles	2.8–4.3 V 150.2 mA·h/g at 1 C, 75.4% retention after 300 cycles	No	[108]

6 总结与展望

如表 3 和图 10 所示,湿法浸出工艺在大规模处理废旧 LIBs 正极材料上具有高效性与实用性。从以下 3 个角度进行总结与展望:

1) 在浸出试剂的选择上,传统酸浸工艺具有广泛的适用性,特别是无机酸(如 H₂SO₄)不仅价格低

廉,同时对废旧 LIBs 中的各类金属能够进行快速溶解,可批量处理各类不同类型的废旧 LIBs,但会产生“三废”污染,对环境造成负面影响,尽管存在更为绿色环保的有机酸,但其高昂的成本在批次处理的工业化进程中仍不具备优势。因此可选取浸出效率高、价格低且对环境友好的酸试剂(特别是有机酸)实现酸浸工艺的优化。

表 3 废旧 LIBs 湿法回收工艺中不同浸出方法的总结分析

Leaching process	Applicability	Operating conditions	Environmental impact	Limitations	Future optimization strategies
Acid leaching	The method has a broad applicability, enabling the rapid dissolution of metals within batteries and demonstrating a high extraction efficiency. It is capable of processing various types of spent LIBs	Commonly used acids, such as H ₂ SO ₄ and HCl, are typically affordable, with established processing infrastructure	The leaching process with inorganic acids generates wastewater, gas emissions, and solid waste, known as ‘three wastes’ pollution, while organic acids are biodegradable and more environmentally friendly	Inorganic acids create major environmental issues, while organic acids lead to higher costs; The purification processes after leachate treatment are quite complex	Select acids with high leaching efficiency and environmental friendliness, particularly organic acids, as the leachate acidic wastewater can be recycled
Ammonia leaching	Selective dissolution of certain metals can be achieved, with higher recovery rates observed for specific metals such as Co	The operational equipment demands are quite stringent	Ammonia solution is relatively environmentally friendly, resulting in minimal environmental pollution	The costs are high, and it’s essential to manage the processing parameters, such as ammonia’s volatility and corrosiveness, which need specialized equipment	Create more efficient processing equipment focused on capturing and recycling evaporated ammonia solutions to reduce costs
Biological leaching	Currently, it remains in the laboratory phase, and the performance of certain battery materials may be suboptimal	Typically conducted at standard temperature and pressure, this procedure shows low energy use and does not require costly chemicals or complex equipment	Utilizing microorganisms to mitigate environmental pollution	Microbial activity is often slow, resulting in longer processing times Identifying microorganisms that target specific metals is crucial to limit their overall use	Cultivating adaptable microorganisms with diverse functions to enable effective leaching in both acidic and alkaline conditions
Deep eutectic solvent leaching	Currently, it remains in the laboratory phase, demonstrating excellent solubility for certain metals	Metal ions readily separate from the solvent, facilitating subsequent processing	Predominantly eco-friendly solvents, characterized by low toxicity or non-toxicity	Preparation costs are high, applied research is underdeveloped, and the process needs optimization	Develop versatile deep eutectic solvents for processing various mixed spent LIBs
Electrochemical leaching	Electrochemical leaching occurs at a significantly faster rate than biological leaching	The leaching process can be controlled by adjusting the current and voltage	Conducting within a relatively closed system to minimize environmental pollution	Intensive energy use, higher equipment costs, and complex operations	Optimize equipment to mitigate the cost burden associated with energy consumption

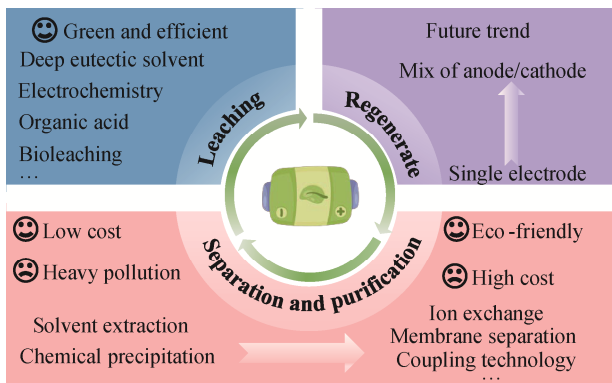


图 10 废旧 LIBs 湿法回收技术总结和未来发展

Fig. 10 Summary and prospect of hydrometallurgy recycling technology for spent LIBs

2) 在设备优化的角度上,氨浸工艺虽然对环境影响较小,金属的选择性浸出效率更高,但其设备成本较高(例如专门收集易挥发的氨气设备)。在未

来创建更高效的处理设备,重点是捕获和回收蒸发氨溶液,以降低成本。而电化学浸出工艺通过调节电流与电压控制设备,能源消耗较大,在未来需要优化设备,减轻与能源消耗相关的成本负担。

3) 在新型工艺的优化上,生物浸出工艺与深共晶溶剂浸出工艺目前仍处于实验室研发阶段。对于生物浸出工艺,特定的微生物培养环境难以控制,需要培养适应性强、功能多样的微生物,能够在强酸和强碱环境下有效浸出。深共晶溶剂的制备成本过高,浸出工艺仍不成熟,需要开发用于处理各种混合废旧 LIBs 的多功能深共晶溶剂。

另外可采取如机械活化、Fe 离子介质、波动辅助等辅助浸出的手段减少浸出剂用量,促进浸出效率与减少浸出成本。而传统的浸出液分离与提纯阶段通常采用化学沉淀与溶剂萃取的策略,但其流程复杂,同时会增加对环境的负担,虽然离子

交换、膜分离等高效的提纯技术具有优势,但其成本仍需要考量。目前废旧 LIBs 主要的回收对象集中在单一的正极材料回收,但在实际应用中通常存在着多种正极材料混合的情况,在预处理的分选除杂过程中会增加其回收成本,因此对于混合正极材料的回收技术仍具有研究的潜力。而对于例如负极、隔膜、集流体等其他组分,尽管其经济效益并没有与正极材料处于同一水平,但对于废旧 LIBs 全组分的闭环回收仍然是未来要努力的方向,以真正做到废旧 LIBs 全组分的资源化与高值化利用。

参考文献:

- [1] WANG J X, MA J, ZHUANG Z F, et al. Toward direct regeneration of spent lithium-ion batteries: A next-generation recycling method[J]. *Chem Rev*, 2024, 124(5): 2839–2887.
- [2] DRISCOLL L L, JARVIS A, MADGE R, et al. Phase-selective recovery and regeneration of end-of-life electric vehicle blended cathodes *via* selective leaching and direct recycling[J]. *Joule*, 2024, 8(10): 2735–2754.
- [3] ZHOU J H, ZHOU X, YU W H, et al. Towards greener recycling: Direct repair of cathode materials in spent lithium-ion batteries[J]. *Electrochem Energy Rev*, 2024, 7(1): 13.
- [4] FAN M, MENG X H, GUO H, et al. Reviving fatigue surface for solid-state upcycling of highly degraded polycrystalline $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ cathodes[J]. *Adv Mater*, 2024, 36(35): e2405238.
- [5] 赖志颖, 赖文斌, 林楚园, 等. 退役动力电池回收利用的现状与碳核算研究进展[J]. *过程工程学报*, 2024, 24(2): 139–150.
LAI Zhiying, LAI Wenbin, LIN Chuyuan, et al. *Chin J Process Eng*, 2024, 24(2): 139–150.
- [6] ZHU X H, LI Y J, GONG M Q, et al. Recycling valuable metals from spent lithium-ion batteries using carbothermal shock method[J]. *Angew Chem Int Ed*, 2023, 62(15): e202300074.
- [7] HU Y, YANG M C, DONG Q Y, et al. Green and sustainable recycling of lithium-ion batteries *via* an ionic liquid-driven cathode reduction method[J]. *Energy Environ Sci*, 2024, 17(12): 4238–4247.
- [8] ZHU P F, JIANG Z P, SUN W, et al. Built-in anionic equilibrium for atom-economic recycling of spent lithium-ion batteries[J]. *Energy Environ Sci*, 2023, 16(8): 3564–3575.
- [9] TANG D, JI G J, WANG J X, et al. A multifunctional amino acid enables direct recycling of spent LiFePO_4 cathode material[J]. *Adv Mater*, 2024, 36(5): e2309722.
- [10] GUO M M, LI K, LIU L Z, et al. Insight into a sustainable application of spent lithium-ion cobaltate batteries: Preparation of a cobalt-based oxide catalyst and its catalytic performance in toluene oxidation[J]. *Ind Eng Chem Res*, 2020, 59(1): 194–204.
- [11] LIANG J X, XUE Y X, GU J N, et al. Sustainably recycling spent lithium-ion batteries to prepare magnetically separable cobalt ferrite for catalytic degradation of bisphenol A *via* peroxymonosulfate activation[J]. *J Hazard Mater*, 2022, 427: 127910.
- [12] LIANG J X, CHEN R C, GU J N, et al. Sustainable recycling of spent ternary lithium-ion batteries *via* an environmentally friendly process: Selective recovery of lithium and non-hazardous upcycling of residue[J]. *Chem Eng J*, 2024, 481: 148516.
- [13] FENG S Y, LI D H, DENG J H, et al. Closed-Loop recovery of spent lithium-ion batteries based on preferentially selective extraction of lithium strategy[J]. *Sep Purif Technol*, 2025, 354: 128953.
- [14] ZHAO J J, ZHOU F Y, WANG H Y, et al. Coupling electrochemical leaching with solvent extraction for recycling spent lithium-ion batteries[J]. *Environ Sci Technol*, 2024.
- [15] FAN M C, ZHAO Y, KANG Y Q, et al. Room-temperature extraction of individual elements from charged spent LiFePO_4 batteries[J]. *Rare Met*, 2022, 41(5): 1595–1604.
- [16] JIANG S Q, XU C, LI X G, et al. Mixed crushing and competitive leaching of all electrode material components and metal collector fluid in the spent lithium battery[J]. *J Environ Manage*, 2024, 358: 120818.
- [17] ZHANG X M, XIE W, ZHOU X L, et al. Study on metal recovery process and kinetics of oxidative leaching from spent LiFePO_4 Li-batteries[J]. *Chin J Chem Eng*, 2024, 68: 94–102.
- [18] TAWONEZVI T, ZIDE D, NOMNQA M, et al. Recovery of $\text{Ni}_x\text{Mn}_y\text{Co}_z(\text{OH})_2$ and Li_2CO_3 from spent Li-ionB cathode leachates using non-Na precipitant-based chemical precipitation for sustainable recycling[J]. *Chem Eng J Adv*, 2024, 17: 100582.
- [19] HAN F, ZHOU L, FANG D F, et al. Alkali-enhanced polyvinylidene fluoride cracking to deeply remove aluminum impurities for regeneration of battery-grade lithium iron phosphate[J]. *Chem Eng J*, 2024, 483: 148973.
- [20] WANG D F, CHEN M, ZHAO J J, et al. Revealing role of oxidation in recycling spent lithium iron phosphate through acid leaching[J/OL]. *Rare Met*, [2024–11–08]. <https://doi.org/10.1007/s12598-024-03007-x>
- [21] MUKAI K, TAKATANI Y, NONAKA T. Mechanisms underlying the acid leaching process for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ with and without H_2O_2 [J]. *Energy Adv*, 2024, 3(5): 1099–1110.
- [22] MA W J, LI S Z, ZHAO Q X, et al. Selective recovery of Li_2CO_3 from single or mixed cathode materials of LIBs using carbonation leaching technology with minor acid[J]. *J Energy Storage*, 2024, 95: 112432.
- [23] YU T T, ZHOU W B, ZHANG Y G, et al. Molecular dynamics simulation study on the interaction mechanisms of leaching solutions and LiCoO_2 surface[J]. *Sep Purif Technol*, 2024, 339: 126596.
- [24] DEL MAR CERRILLO-GONZALEZ M, VILLEN-GUZMAN M, RIVAS-BASCON A, et al. A comparison of batch and semi-batch reactors for leaching battery cathodes (LiCoO_2) under controlled addition of HCl and H_2O_2 [J]. *Hydrometallurgy*, 2024, 227: 106334.
- [25] SONOC A, MARTHI R, JESWIET J. A zero-liquid discharge process to recover all critical metals from spent NCM111 cathode material of end-of-life lithium-ion batteries: Statistically optimized leaching with formic acid and *in situ* crystallization[J]. *Hydrometallurgy*, 2024, 230: 106362.
- [26] RAUTELA R, YADAV B R, KUMAR S. Enhancing the efficiency of metals extraction from waste lithium-ion batteries through glycine leaching using response surface methodology for economic feasibility[J]. *J Clean Prod*, 2024, 447: 141602.
- [27] SAHU S, AGRAWALA M, PATRA S R, et al. Synergistic approach for selective leaching and separation of strategic metals from spent lithium-ion batteries[J]. *ACS Omega*, 2024, 9(9): 10556–10565.
- [28] OKONKWO E G, WHEATLEY G, LIU Y, et al. Metal recovery from spent lithium-ion batteries cathode materials: Comparative study of sugar-based reductants[J]. *J Hazard Mater Lett*, 2024, 5: 100104.
- [29] ZHAO T Y, MAHANDRA H, CHOI Y, et al. A clean and sustainable method for recycling of lithium from spent lithium iron phosphate

- battery powder by using formic acid and oxygen[J]. *Sci Total Environ*, 2024, 920: 170930.
- [30] ZHANG J Z, DING Y, SHI H, et al. Selective recycling of lithium from spent $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ cathode *via* constructing a synergistic leaching environment[J]. *J Environ Manage*, 2024, 352: 120021.
- [31] BHAGASKARA A, SAPUTRA D A, SAVIOLA A J, et al. Recycling of nickel metal from spent nickel-manganese-cobalt (NMC) cathode batteries using $\text{H}_3\text{PO}_4\text{-H}_2\text{C}_2\text{O}_4$ solution combination as an efficient leaching agent[J]. *Case Stud Chem Environ Eng*, 2024, 10: 100844.
- [32] YU J C, MA B Z, QIU Z J, et al. Separation and recovery of valuable metals from ammonia leaching solution of spent lithium-ion batteries[J]. *ACS Sustainable Chem Eng*, 2023, 11(26): 9738–9750.
- [33] YANG C, CHEN G J, XU L, et al. Facile fabrication of nickel-cobalt oxide for efficient oxygen evolution reaction from ammonia leaching solution of spent lithium-ion batteries[J]. *Int J Hydrog Energy*, 2024, 71: 1334–1341.
- [34] YE L, XU Z L, GONG H Q, et al. An ultra-fast reaction process for recycling lithium ion batteries *via* galvanic cell interaction[J]. *Chem Sci*, 2024, 16(1): 297–309.
- [35] YUN S, JUNG H, LEE H J, et al. Bioleaching of valuable metals from three cathode active materials comprising lithium nickel cobalt manganese (NCM) oxide using indigenous microorganisms[J]. *J Ind Eng Chem*, 2024, 135: 552–560.
- [36] YANG Z D, CHEN L D, XU S C, et al. Tailored biolixiviation of spent LiCoO_2 cathode batteries for sustainable metal recovery: Effects of consortia adaptation and particle size[J]. *Chem Eng Sci*, 2025, 302: 120858.
- [37] NASERI T, MOUSAVI S M. Improvement of Li and Mn bioleaching from spent lithium-ion batteries, using step-wise addition of biogenic sulfuric acid by *Acidithiobacillus thiooxidans*[J]. *Heliyon*, 2024, 10(18): e37447.
- [38] LOU L, LIU X C, WANG Y Y, et al. Achieving reusability of leachate for multi-element recovery of the discarded $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ cathode by regulating the co-precipitation coefficient[J]. *Chin Chem Lett*, 2024, 3: 109726.
- [39] WANG Z J, HU T, LOU L, et al. Realizing lean-leachate recycling of spent lithium nickel oxides by dynamically stabilizing the hole-mediated diffusion kinetics[J]. *ACS Appl Mater Interfaces*, 2024, 16(18): 23160–23168.
- [40] ZHENG S M, XU S, WANG Z H, et al. Efficient leaching of valuable metals from spent lithium-ion batteries using green deep eutectic solvents: Process optimization, mechanistic analysis, and environmental impact assessment[J]. *J Clean Prod*, 2024, 480: 144128.
- [41] LI B, LI C P, WANG J S, et al. High-efficiency leaching of valuable metals from waste lithium-ion ternary batteries under mild conditions using green deep eutectic solvents[J]. *Green Chem*, 2025, 27(1): 163–178.
- [42] YANG L M, GAO Z, LIU T, et al. Direct electrochemical leaching method for high-purity lithium recovery from spent lithium batteries[J]. *Environ Sci Technol*, 2023, 57(11): 4591–4597.
- [43] CHEN M, GUO L F, LI Y Y, et al. Highly selective extraction of lithium from spent NCM cathode powder reconstructive electrode by acid-free electrochemical process[J]. *Energy Fuels*, 2024, 38(6): 5558–5567.
- [44] TIAN S C, CAO Y M, DONG L P, et al. Selective recovery of lithium from spent LiFePO_4 powders with electrochemical method[J]. *J Environ Chem Eng*, 2024, 12(3): 112871.
- [45] CHEN J, MA E, ZHANG C L, et al. Mechanism and technological method of leaching metals from waste lithium-ion batteries by synergistic action of natural organic reductants and mechanochemical method[J]. *Sep Purif Technol*, 2025, 353: 128371.
- [46] HE T, ZHAO J X, CHEN D X, et al. Self-actuated leaching and integrated separation of spent lithium-ion batteries cathode and anode sheets[J]. *Sep Purif Technol*, 2024, 345: 127396.
- [47] DE OCA D M M, SHI M, DIAZ L A, et al. Electrochemical leaching of spent LIBs: Kinetics, novel reactor, and modeling[J]. *Sustain Mater Technol*, 2024, 40: e00898.
- [48] WEI N, HE Y Q, ZHANG G W, et al. A sustainable strategy for recovering spent cathode materials based on *in situ* thermal reduction and electrically driven leaching[J]. *Sep Purif Technol*, 2025, 354: 129543.
- [49] NIU Y, SHI D, CHENG X Y, et al. A closed-loop coupling process of leaching and solvent extraction for Li_2CO_3 and FePO_4 recovery from spent LiFePO_4 [J]. *Sustain Mater Technol*, 2024, 39: e00827.
- [50] LIU Z H, LIAO X J, ZHANG Y M, et al. A highly efficient process to enhance the bioleaching of spent lithium-ion batteries by bifunctional pyrite combined with elemental sulfur[J]. *J Environ Manage*, 2024, 351: 119954.
- [51] BORRA V L, JENA A, SISTLA N S, et al. Synergetic recycling of permanent magnet and Li-ion battery cathode material for metals recovery[J]. *Sustain Mater Technol*, 2024, 41: e01043.
- [52] KIM J, NWE H H, YOON C S. Enhanced bioleaching of spent Li-ion batteries using A. ferrooxidans by application of external magnetic field[J]. *J Environ Manage*, 2024, 367: 122012.
- [53] NSHIZIRUNGU T, RANA M, JO Y T, et al. Ultrasound-assisted sustainable recycling of valuable metals from spent Li-ion batteries *via* optimisation using response surface methodology[J]. *J Environ Chem Eng*, 2024, 12(2): 112371.
- [54] OKONKWO E G, WHEATLEY G, LIU Y, et al. A cavitation enabled green leaching of metals from spent lithium-ion batteries[J]. *Chem Eng Process Process Intensif*, 2024, 202: 109850.
- [55] LI H F, BERBILLE A, ZHAO X, et al. A contact-electro-catalytic cathode recycling method for spent lithium-ion batteries[J]. *Nat Energy*, 2023, 8: 1137–1144.
- [56] LIN M Y, ZHANG J L, XU C J, et al. Two targets, one strike: Efficient recovery of lithium and simultaneous removal of impurities from spent LFP batteries *via* ferric ions assisted air oxidation method[J]. *Sep Purif Technol*, 2025, 355: 129558.
- [57] DING W, BAO S X, ZHANG Y M, et al. Sustainable regeneration of high-performance cathode materials from spent lithium-ion batteries through magnetic separation and coprecipitation[J]. *J Clean Prod*, 2024, 438: 140798.
- [58] LI S Y, ZHANG W C, XIA Y, et al. Enhanced reducing capacity of citric acid for lithium-ion battery recycling under microwave-assisted leaching[J]. *Waste Manag*, 2024, 189: 23–33.
- [59] KANG S Y, OU J T, WANG X, et al. Effect analysis on recycling of cathode material from spent ternary lithium-ion batteries *via* supercritical water oxidation and acid-leaching[J]. *J Supercrit Fluids*, 2024, 211: 106297.
- [60] LIU G Q, LIU Z J, GU J, et al. Facile and sustainable recovery of spent LiFePO_4 battery cathode materials in a $\text{Ca}(\text{ClO})_2$ system[J]. *Green Chem*, 2024, 26(6): 3317–3328.
- [61] 曾诗涵, 张继享, 吴燕芳, 等. 退役动力电池磷酸铁锂正极材料的应用现状和回收利用技术[J]. *再生资源与循环经济*, 2022, 15(3): 28–32.

- ZENG Shihan, ZHANG Jixiang, WU Yanfang, et al. *Recycl Resour Circ Econ*, 2022, 15(3): 28–32.
- [62] XIAO F Y, LAI W B, ZENG S H, et al. Facile fabrication of $\text{FePO}_4\text{-V}_2\text{O}_5$ -graphene oxide recovered from spent LiFePO_4 batteries as high-performance cathode for lithium/sodium-ion batteries[J]. *Adv Sustain Syst*, 2024, 8(8): 2400098.
- [63] ZENG S H, XU Q X, JIN H J, et al. A green strategy towards fabricating FePO_4 -graphene oxide for high-performance cathode of lithium/sodium-ion batteries recovered from spent batteries[J]. *J Electroanal Chem*, 2022, 913: 116287.
- [64] TIAN B Y, LI J Z, ZHAO J, et al. Humic acid-mediated mechanism for efficient biodissolution of used lithium batteries[J]. *J Hazard Mater*, 2024, 477: 135400.
- [65] WANG Z, LI M, FU B, et al. Recycling cobalt from spent lithium-ion batteries for designing the novel cobalt nitride followers: Towards efficient overall water splitting and advanced zinc-air batteries[J]. *J Colloid Interface Sci*, 2024, 662: 218–230.
- [66] CARENA E, MORINA R, BRUGNETTI G, et al. The recycling of lithium-ion batteries LiCoO_2 cathode: Balancing sustainability and efficiency[J]. *J Chem Educ*, 2024, 101(5): 2124–2133.
- [67] MARTINS L S, ROVANI S, BOTELHO A B Jr, et al. Sustainable approach for critical metals recovery through hydrometallurgical processing of spent batteries using organic acids[J]. *Ind Eng Chem Res*, 2023, 62(44): 18672–18682.
- [68] LI Y J, DONG L P, SHI P, et al. Selective recovery of lithium from lithium iron phosphate[J]. *J Power Sources*, 2024, 598: 234158.
- [69] JOSHI B, PRASETYO E, BANDYOPADHYAY S. Selective lithium recovery from pyrolyzed black mass through optimized caustic leaching[J]. *J Environ Chem Eng*, 2024, 12(5): 113787.
- [70] KANG X C, ZHANG X X, LIU S, et al. Selective recovery of lithium from used lithium-ion batteries spent *via* grain boundary reconstruction reaction[J]. *Sep Purif Technol*, 2025, 356: 129726.
- [71] SU F Y, ZHOU X Y, LIU Y K, et al. A Fe(III)-driven strategy for efficient closed-loop recovery of critical metals from spent $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ powder[J]. *Chem Eng J*, 2024, 493: 152297.
- [72] PEI S Z, YAN S X, CHEN X P, et al. Novel electrochemical process for recycling of valuable metals from spent lithium-ion batteries[J]. *Waste Manag*, 2024, 188: 1–10.
- [73] YAO Q, XIAO F Y, LIN C Y, et al. Regeneration of spent lithium manganate into cation-doped and oxygen-deficient MnO_2 cathodes toward ultralong lifespan and wide-temperature-tolerant aqueous Zn-ion batteries[J]. *Battery Energy*, 2023, 2(4): 20220065.
- [74] ZHAO R Z, SUN H, LIU L J, et al. A new solvent extraction technology and mechanism for the separation and recovery of Li^+ using benzene sulfonamide acid substance[J]. *Sep Purif Technol*, 2025, 356: 129913.
- [75] QING J L, WU X S, ZENG L, et al. High-efficiency recovery of valuable metals from spent lithium-ion batteries: Optimization of SO_2 pressure leaching and selective extraction of trace impurities[J]. *J Environ Manag*, 2024, 356: 120729.
- [76] HAN Y X, CHEN J, LI H L, et al. Selective recovery of transition metals from spent lithium-ion batteries leachate with Ni synergistic extraction system[J]. *J Environ Chem Eng*, 2024, 12(5): 113321.
- [77] LI X H, BENSTEAD M, PEETERS N, et al. Recycling of metals from LiFePO_4 battery cathode material by using ionic liquid based-aqueous biphasic systems[J]. *RSC Adv*, 2024, 14(13): 9262–9272.
- [78] MUŠOVIĆ J, TEKİĆ D, MARIĆ S, et al. Sustainable recovery of cobalt and lithium from lithium-ion battery cathode material by combining sulfate leachates and aqueous biphasic systems based on tetrabutylphosphonium-ionic liquids[J]. *Sep Purif Technol*, 2024, 348: 127707.
- [79] GONG S Y, DONG E H, LIU B G, et al. Eco-friendly closed-loop recycling of nickel, cobalt, manganese, and lithium from spent ternary lithium-ion battery cathodes[J]. *Sep Purif Technol*, 2024, 348: 127771.
- [80] WESSELBORG T, ASUMALAHTI S, VIROLAINEN S, et al. Design of a continuous ion exchange process in battery metals recycling: From single column experiments towards a simulated moving bed configuration[J]. *Hydrometallurgy*, 2024, 228: 106361.
- [81] LEI Q Y, ZHOU K G, ZHANG X K, et al. Selective extraction of valuable metals from the organic leachate of spent $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ battery through a sequential co-precipitation-resin adsorption approach[J]. *Sep Purif Technol*, 2025, 353: 128501.
- [82] HUO X, WANG J Y, TANG X, et al. Stepwise separation and recovery of metal ions from waste $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ batteries using a NaA zeolite[J]. *ACS Sustain Resour Manag*, 2024, 1(5): 970–977.
- [83] PENG Z J, LU Q C, ZHU Z H, et al. Efficient and green recovery of lithium from spent lithium-ion batteries based on a multipotential field membrane process intensification[J]. *ACS Sustainable Chem Eng*, 2024, 12(47): 17249–17262.
- [84] TROITSKIY V A, PASECHNAYA E L, SMIRNOVA N V, et al. Lithium recycling from artificial leachate of spent lithium-ion batteries using track-etched membranes for hybrid electrobaromembrane method[J]. *J Water Process Eng*, 2024, 66: 105919.
- [85] HE S, ZUO Q Y, SHI H, et al. Direct recovery of high-purity lithium *via* nanofiltration membranes from leaching solution of spent lithium batteries[J]. *Resour Conserv Recycl*, 2024, 210: 107846.
- [86] FOO Z H, LIU S W, KANIAS L, et al. Positively-coated nanofiltration membranes for lithium recovery from battery leachates and salt-lakes: Ion transport fundamentals and module performance[J]. *Adv Funct Materials*, 2024, 34(48): 2408685.
- [87] QU G R, YANG J Q, RAN Y X, et al. Adsorption performance and mechanism of TiO_2/PVDF -based lithium-ion imprinted membrane in leaching solution of spent lithium-ion batteries[J]. *J Clean Prod*, 2024, 442: 140982.
- [88] ZHU J Y, ASADI A, KANG D X, et al. Bipolar membranes electrodialysis of lithium sulfate solutions from hydrometallurgical recycling of spent lithium-ion batteries[J]. *Sep Purif Technol*, 2025, 354: 128715.
- [89] CHEN H, LIAO L Y, DING Y X, et al. Feasible route for the regeneration of cathode materials from spent lithium-ion batteries *via* reduction leaching and in-site precipitation[J]. *J Power Sources*, 2024, 598: 234155.
- [90] ZHOU M M, SHEN J, DUAN Y, et al. The Le Chatelier's principle enables closed loop regenerating ternary cathode materials for spent lithium-ion batteries[J]. *Energy Storage Mater*, 2024, 67: 103250.
- [91] KIM S, PARK S, KIM D, et al. Closed-loop resynthesis of LiNiCoAlO_2 cathode active materials from the industrial leachate of spent li-ion batteries[J]. *Chem Eng J*, 2024, 494: 153199.
- [92] ZHANG X H, YANG S L, DENG C Q, et al. Selective recovery of metals in spent batteries by electrochemical precipitation to cathode material for sodium-ion batteries[J]. *Heliyon*, 2024, 10(5): e27127.
- [93] LEI S Y, ZHAO W Q, LI J X, et al. For elements-utilization regeneration of spent LiFePO_4 : Designed basic precursors for advanced polycrystal electrode materials[J]. *Energy Storage Mater*, 2025, 74:

- 103863.
- [94] FU D J, ZHOU W, LIU J L, et al. A facile route for the efficient leaching, recovery, and regeneration of lithium and iron from waste lithium iron phosphate cathode materials[J]. *Sep Purif Technol*, 2024, 342: 127069.
- [95] ZHOU M M, SHEN J, ZUO Y Z, et al. The Fischer-lactonization-driven mechanism for ultra-efficient recycling of spent lithium-ion batteries[J]. *Angew Chem Int Ed*, 2025, 137(2): e202414484.
- [96] WANG J Z, HUANG K, DONG H L, et al. A green process for recycling and synthesis of cathode materials LiMn_2O_4 from spent lithium-ion batteries using citric acid[J]. *RSC Adv*, 2022, 12(36): 23683–23691.
- [97] YU L, BAI Y C, ESSEHLI R, et al. Efficient separation and coprecipitation for simplified cathode recycling[J]. *Energy Storage Mater*, 2023, 63: 103025.
- [98] ZHANG Y, YU M, GUO J M, et al. Recover value metals from spent lithium-ion batteries via a combination of *in situ* reduction pretreatment and facile acid leaching[J]. *Waste Manag*, 2023, 161: 193–202.
- [99] MA R F, TAO S Y, SUN X, et al. Pathway decisions for reuse and recycling of retired lithium-ion batteries considering economic and environmental functions[J]. *Nat Commun*, 2024, 15(1): 7641.
- [100] TAO S Y, MA R F, ZHAO Z X, et al. Generative learning assisted state-of-health estimation for sustainable battery recycling with random retirement conditions[J]. *Nat Commun*, 2024, 15: 10154.
- [101] TAO S Y, ZHANG M T, ZHAO Z X, et al. Non-destructive degradation pattern decoupling for early battery trajectory prediction via physics-informed learning[J]. *Energy Environ Sci*, 2025, 18(3): 1544–1559.
- [102] TAO S Y, LIU H Z, SUN C B, et al. Collaborative and privacy-preserving retired battery sorting for profitable direct recycling via federated machine learning[J]. *Nat Commun*, 2023, 14(1): 8032.
- [103] SUN Y H, YANG H J, LI J, et al. A large volume and low energy consumption recycling strategy for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ from spent ternary lithium-ion batteries[J]. *J Power Sources*, 2024, 602: 234407.
- [104] CHU W, ZHANG Y L, CHEN X, et al. Synthesis of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ from mixed cathode materials of spent lithium-ion batteries[J]. *J Power Sources*, 2020, 449: 227567.
- [105] HUANG Z X, LIU X, ZHENG Y, et al. Boosting efficient and low-energy solid phase regeneration for single crystal $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ via highly selective leaching and its industrial application[J]. *Chem Eng J*, 2023, 451: 139039.
- [106] FANG J H, DING Z P, LING Y, et al. Green recycling and regeneration of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ from spent Lithium-ion batteries assisted by sodium sulfate electrolysis[J]. *Chem Eng J*, 2022, 440: 135880.
- [107] ZHOU H X, HU Q, LI L Q, et al. Endogenous advanced oxidation process with peracetic acid for recycling spent LiFePO_4 batteries[J]. *Chem Eng Sci*, 2024, 295: 120202.
- [108] LI L, BIAN Y F, ZHANG X X, et al. Process for recycling mixed-cathode materials from spent lithium-ion batteries and kinetics of leaching[J]. *Waste Manag*, 2018, 71: 362–371.

A Review on Hydrometallurgy Recycle and Regeneration Technology of Cathode Materials for Spent Lithium-ion Batteries

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Extended Abstract

Spent lithium-ion batteries contain rare metals such as lithium, cobalt, nickel and manganese, which are limited and unevenly distributed. Through recovery, we can effectively reduce the dependence on the exploitation of new mineral resources and realize the sustainable utilization of resources. It can reduce the cost of raw materials for the production of new batteries, and the development of the battery recycling industry can create new job opportunities and promote economic growth. As lithium-ion batteries contain heavy metals and other harmful substances, if discarded at will, these substances may seep into the soil and water sources, causing serious environmental pollution. The energy consumption in the process of battery production and recycling will produce greenhouse gases. If not handled properly, it may cause fire or explosion due to internal short circuit, overheating and other reasons, resulting in safety accidents. Therefore, effective recycling can reduce the energy consumption needed for the production of new batteries, thereby reducing greenhouse gas emissions. In terms of policies and regulations, many countries and regions have laws and regulations on e-waste disposal, which require the recycling of decommissioned batteries. Enterprises can show their sense of social responsibility and enhance their corporate image by recycling retired batteries. This can not only promote the development of related environmental protection technology and material science, establish a perfect battery recycling system, but also help to form a complete closed-loop industry chain from battery production to recycling. In a word, the recycling of spent lithium-ion batteries not only is of great significance to environmental protection and resource conservation, but also has a far-reaching impact on promoting economic development, meeting the requirements of laws and regulations, and promoting corporate social responsibility. With the popularity of electric vehicles and other portable electronic devices, the number of retired batteries will continue to increase, and the importance of battery recycling will become more and more prominent.

Recycling the valuable metal resources of spent lithium-ion batteries can generate significant economic benefit. Among various recycling technologies, hydrometallurgy reveals better application potential due to its high maturity and recovery rate. This review focus on the development of hydrometallurgy, including the methods of leaching, separation, purification and re-synthesis of spent cathode materials. The first part introduces the leaching strategies, using acid, ammonia, deep eutectic solvent, bioleaching, and electrochemical leaching, as well as the auxiliary methods for such methods. The second part summarized the purification technologies for the leaching solution and the following re-synthesis process, while the former includes the chemical precipitation method, solvent extraction method, ion exchange method, and membrane separation method and the latter contains the high temperature solid state method and sol-gel method. In the third part, the bottlenecks of hydrometallurgy are summarized, and possible solutions are provided for the development of hydrometallurgy regeneration technology.

Summary and prospects Hydrometallurgy has high efficiency and practicability in the large-scale application of recycling the cathode materials of spent lithium-ion battery. However, it consumes a large number of chemical reagents during the leaching process, generating pollutants and arousing attention. Therefore, the key issue is to reduce the negative environmental impact caused by hydrometallurgy. The selection of green and efficient leaching technology is beneficial to reduce the production of “three wastes” pollutants in the hydrometallurgy recycle technology, in which the environment-friendly organic acid has the characteristics of both leaching agent and chelating agent, promising to partly replace the inorganic acid leaching in the future. Using the microorganisms to leaches the spent lithium-ion batteries is an environmentally friendly and cheap method, which can design a targeted leaching process by adjusting its own redox properties. However, its strict cultivation environment and inefficiency have become a major difficulty in industrialization. Compared with the traditional acid leaching technology, deep eutectic solvent technology and electrochemistry technology still do not have the advantage in cost. For different cathode materials, auxiliary leaching methods such as mechanical activation, Fe ion medium and wave assistance can be adopted to reduce the amount of leaching agent, increasing the leaching efficiency and economic benefit. The traditional chemical precipitation and solvent extraction for separating and purifying often reveal a complex process, increasing the burden on the environment. The advanced purification technologies such as ion exchange and membrane separation generate positive effects on the environment, its cost still needs to be considered. Besides, enormous efforts have been paid on recycling the single cathode materials. However, the spent cathode materials collected from the market often consisted of a mixture of different cathode materials, which trend to increase the cost of pretreatment and separation process. Therefore, recycling technology for mixed cathode materials should be studied. For recycling other components used in lithium-ion batteries, such as anode materials, separator, current collector and so on, although it generates lower economic benefits than that of cathode materials, the closed-loop recycle of all components of spent lithium-ion batteries is still important in the future, which realizes high-value and deeply utilization of the whole components of spent lithium-ion batteries.

Keywords spent lithium-ion batteries; cathode materials; hydrometallurgy; recycle; regeneration