

Easily recyclable lithium-ion batteries: Recycling-oriented cathode design using highly soluble LiFeMnPO_4 with a water-soluble binder

Hao Du¹ | Yuqiong Kang¹ | Chenglei Li¹ | Yun Zhao¹  | John Wozny² | Tao Li² | Yao Tian¹ | Jian Lu¹ | Li Wang³ | Feiyu Kang¹ | Naser Tavajohi⁴ | Baohua Li¹

¹Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, China

²Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois, USA

³Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China

⁴Department of Chemistry, Umeå University, Umeå, Sweden

Correspondence

Yun Zhao and Baohua Li, Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China.
Email: yzhao.zjut@hotmail.com and libh@mail.sz.tsinghua.edu.cn

Li Wang, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China.
Email: wang-l@tsinghua.edu.cn

Funding information

Key-Area Research and Development Program of Guangdong Province, Grant/Award Number: 2020B090919003

Abstract

Recycling lithium-ion batteries (LIBs) is fundamental for resource recovery, reducing energy consumption, decreasing emissions, and minimizing environmental risks. The inherited properties of materials and design are not commonly attributed to the complexity of recycling LIBs and their effects on the recycling process. The state-of-the-art battery recycling methodology consequently suffers from poor recycling efficiency and high consumption from issues with the cathode and the binder material. As a feasibility study, high-energy-density cathode material LiFeMnPO_4 with a water-soluble polyacrylic acid (PAA) binder is extracted with dilute hydrochloric acid at room temperature under oxidant-free conditions. The cathode is wholly leached with high purity and is suitable for reuse. The cathode is easily separated from its constituent materials and reduces material and energy consumption during recycling by 20% and 7%, respectively. This strategy is utilized to fabricate recyclable-oriented LiFeMnPO_4 /graphite LIBs with a PAA binder and carbon paper current collector. Finally, the limitation of the solubility of the binder is discussed in terms of recycling. This research hopefully provides guidance for recycling-oriented design for the circular economy of the LIB industry.

KEYWORDS

battery design, easily recyclable batteries, LiFeMnPO_4 , lithium-ion batteries, recycling

Hao Du, Yuqiong Kang, and Chenglei Li contributed equally to this work.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2023 The Authors. *Battery Energy* published by Xijing University and John Wiley & Sons Australia, Ltd.

1 | INTRODUCTION

Battery design oriented toward recycling is required to comply with the principles of a circular economy for the lithium-ion battery (LIB) industry.¹ The typical LIB cell is complex and comprises various valuable metals, carbon-based materials, and fluorinated derivatives.² LIB cell complexity presents significant challenges to material separation and cathode leaching, making it difficult to recycle while reducing recycling efficiency.³ Individual components of spent LIBs can be easily separated mechanically. Breaking each component further down to recover its constituent materials in pure form is less straightforward.⁴ For example, the disassembly of cathodes is hindered by the properties of the binder and cathode materials.^{5–7} Recycling research on LIB has emphasized recovering Al foil and cathode materials over other valuable materials (e.g., conductive agents). The LIB recycling processes are costly in terms of material and energy consumption, reducing profitability, and having deleterious effects on the environment.⁸ Recycling 1 tonne of LiFePO₄ cells using modern recycling methods would require 10 kL of 1 M HCl, 10 kL of 1 M H₂O₂, and 54.73 kJ of energy, with a projected cost of ~\$2400 (16,400 Chinese yuan [CNY]). The primary recovered material would be approximately 55 kg of Li₂CO₃, valued at ~\$3400 (23,600 CNY) at the current market price.^{9–12} Unfortunately, recycling LiFePO₄ may become commercially unviable with labor and processing costs, as the profitability is strongly linked to the lithium salts' market price. If the lithium salts' prices stabilize, the revenue recovered lithium salts could depreciate as low as ~\$1400 (9600 CNY). Approaches to combat the dependency on lithium salt would require reduced labor and processing costs. This can be achieved by designing the next generation of LIBs that are easily separated and oriented for recycling to further support the LIB industry's development.

Next-generation LIBs will require higher energy-density cathode materials to meet the increasing energy demands while being easily recyclable. Cutting-edge research on promising cathode materials based on olivine LiFePO₄, layered LiCoO₂, and LiNi_xCo_yMn_zO₂ is being developed and explored. LiFePO₄ has been one of the most widely used modern cathode materials because of its low cost, favorable operating parameters, and safety. Mn has emerged as a supplementary material for Fe in LiFePO₄ LIBs, increasing energy density by up to 20% and raising the output voltage from 3.5 to 4.1 V (Figure 1A).^{13–15} The theoretical energy density of a LiFeMnPO₄ battery is comparable to layered cathode materials and dramatically exceeds the performance of

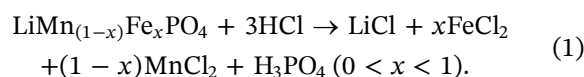
LiFePO₄ batteries. The precursor of LiFeMnPO₄ materials is cheaper than Ni and Co, which could enable a more sustainable LIB production (Figure 1B).

Herein, LiFe_{0.3}Mn_{0.7}PO₄ exemplifies a high-energy-density cathode material that can be easily recycled by leaching with hydrochloric acid (HCl) at room temperature under oxidant-free conditions (Figure 1C). The effects of the HCl concentration, leaching duration, and solid-liquid (S/L) ratio on the effects of leaching efficiencies for Li, Fe, Mn, and P were investigated. Results indicate that the cathode material is easily recycled with a water-soluble binder,^{16,17} enabling quick recovery and reuse of the current collector, the cathode material, and the residual carbon materials.

2 | RESULTS AND DISCUSSIONS

2.1 | LiFeMnPO₄ leaching

The results of leaching experiments using LiFeMnPO₄ are shown in Figure 2. Various HCl concentrations (0.5, 1.0, 2.0, and 3.0 mol/L) were tested at room temperature as a solvent for LiFeMnPO₄ leachants, loading 20 g/L with a 1-h leaching time. Figure 2A–D demonstrates that the leaching efficiencies for Li and Mn were around 94% when using 0.5 mol/L HCl, while for Fe and P, they were around 90%. Increasing HCl concentrations improved all elements' leaching efficiencies to 100%, demonstrating that LiFeMnPO₄ is readily recycled. The chemical equation of the leaching process is in Equation (1). According to Equation (1), $\Delta fG = 1152.27x - 952.8$ ($0 < x < 1$). Given $x = 0.3$, the Gibbs free energy of formation for this reaction is -607.12 kJ/mol, which means this reaction can occur at room temperature (Table S1).



The effect of varying the S/L ratio on Li, Fe, Mn, and P leaching efficiency was investigated to evaluate the feasibility of industrial-scale LiFeMnPO₄ recovery. The time to effectively leach out the metals was evaluated with various solvent exposure times (10, 30, 60, 120, and 180 min) at 1.0 mol/L HCl. Leaching readily occurs with 68.0%–75.5% leaching efficiencies within 10 min of HCl solvent exposure at 1.0 mol/L HCl (Figure 2E–H). Extending the reaction time to 30 min increases the Fe and Mn leaching efficiencies to ~99.0%, while those of Li and P were 87.2% and 94.6%, respectively. Complete dissolution of all elements was achieved within one hour. The leaching efficiency remained nearly 100% for all elements when the S/L ratio was

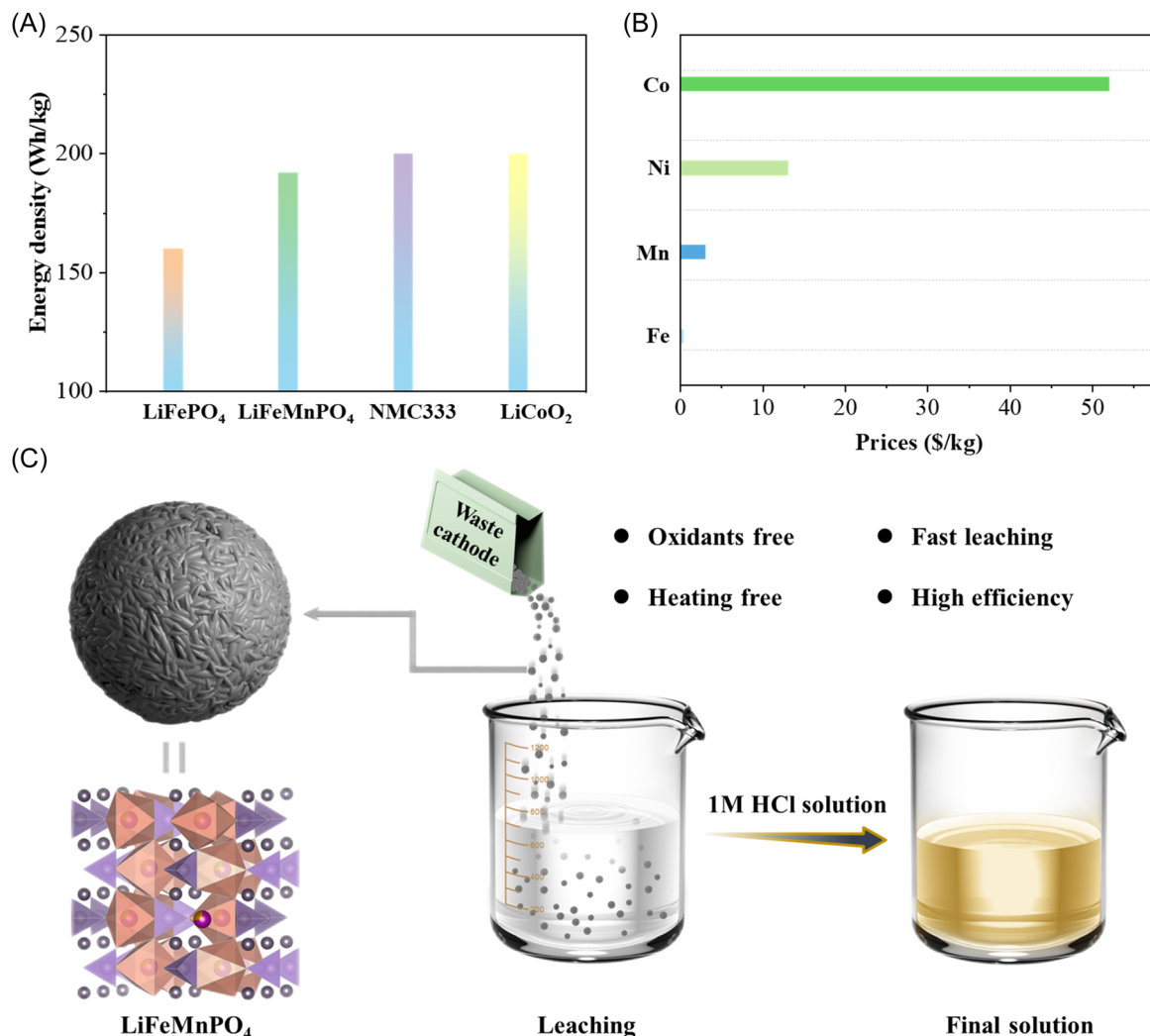


FIGURE 1 Properties of LiFeMnPO₄ and its recycling. (A) The energy densities of LIB cells (Wh/kg) utilizing various cathode materials. (B) Prices of metal elements in LiFeMnPO₄ LIBs. (C) The schematic for the leaching process of LiFeMnPO₄ and its advantages.

between 10 and 30 g/L. However, when the S/L ratio was 40 g/L, it decreased the leaching efficiency of Li, Fe, Mn, and P below 90% (Figure 2I,J). The decreased leaching efficiency may be potentially attributed to Le Châtelier's principle, where the product of leachants shifts the reaction's direction back toward reactants preventing equilibrium from moving toward leaching.¹⁸ LiFeMnPO₄ leaching was optimally performed using HCl concentrations higher than 1.0 mol/L, with an S/L ratio of less than 30 g/L and a leaching time more than 1-h. Under these conditions, the residual carbon material obtained after leaching was very pure, with Li, Fe, Mn, and P content below 0.02 ppm (Figure 2K). Separate experiments using 2.0 mol/L H₂SO₄ as the leachant, instead of HCl, resulted in Li's complete dissolution but were poor at recovering Fe at ~20% leaching efficiency (Figure 2L).

2.2 | Cathode separation

The excellent leaching properties of LiFeMnPO₄ suggest that it could be used to create easily recycled cathodes for enhanced recyclability. Separating traditional cathode materials is generally inherent to using polyvinylidene fluoride (PVDF) as a binder due to poor solubility in water and organic solvents. Water-soluble polyacrylic acid (PAA) was explored as a potential cathode binder (Figure 3A,B) to avoid the solubility issues of PVDF; this allows the cathode materials to be separated from the Al foil simply by washing with water, as shown in Figure 3B.

The cathode materials that remain after removing the Al foil require further processing to separate the active cathode material from the residual carbon materials, both of which are valuable. Conventional

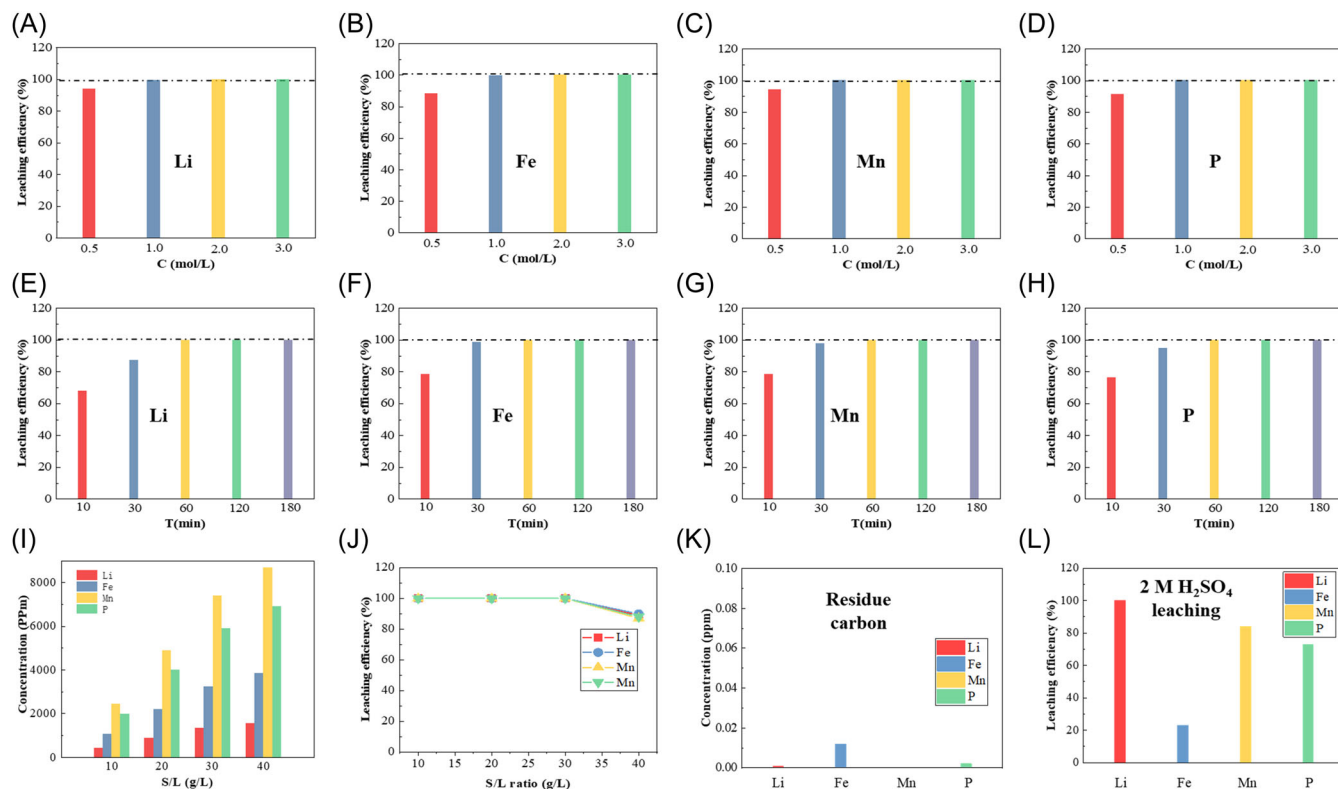


FIGURE 2 Leaching of LiFeMnPO₄. (A–D) The effects of HCl concentrations on leaching efficiencies for Li, Fe, Mn, and P. (E–H) The results of leaching time on leaching efficiencies for Li, Fe, Mn, and P. (I, J) The effects of the solid/liquid (S/L) ratio on leaching efficiencies for Li, Fe, Mn, and P. (K) Li, Fe, Mn, and P content in the residual carbon after LiFeMnPO₄ leaching. (L) Li, Fe, Mn, and P leaching efficiencies using 2 M H₂SO₄ as the leachant.

LIB cathodes comprise the active cathode material, PVDF, and a conductive nanomaterial. While the majority of the active cathode material can generally be recovered by acid leaching, residual metal elements can significantly affect the performance and properties of the recovered material if the leaching efficiency is below 100%. Furthermore, the poor solubility properties of PVDF binders increase the complexity of recovering the conductive nanomaterial. Utilizing more soluble cathode active materials and binders thus facilitates the recycling of the residual carbon materials. Figure 3 illustrates that the residual material obtained after removing the Al foil and water-soluble binder from LiFeMnPO₄ cathodes consists of carbon-coated LiFeMnPO₄ particles mixed with the conductive agent. Due to strong interactions between these materials, this mixture cannot be separated based on density differences. However, the residual LiFeMnPO₄ can be removed by completely leaching the active cathode material, leaving only carbon materials. While these residual carbon materials include the conductive nanomaterial and nano-coating layers from LiFeMnPO₄ particles, the mixture could theoretically be repurposed as a conductive agent.

Images with the electron microscope were used to evaluate the practicality of reusing the recovered carbon materials. As shown in Figure 3B, with the assistance of a water-soluble PAA binder, cathode materials are readily separated from the Al foil physically. Figure 3C shows that the LiFeMnPO₄ particles were coated with graphene layers and that the graphene remaining after leaching contained no detectable Fe, Mn, or P. Accordingly, the residual carbon material obtained from recycled cathodes after leaching was highly pure: Figure 3D shows that it consisted of the conductive agent (super P) and graphene layers from LiFeMnPO₄ particles, with no detectable metallic impurities at the micron scale. This material's energy-dispersive X-ray spectroscopy analyses confirmed the absence of characteristic peaks for Fe and P at 0.8 and 2.0 keV, respectively (Figure 3E).

The only noncarbon peak present is a minor peak corresponding to trace quantities of O (0.53 keV) at the edges of the carbon material and indicating the potential suitability of reusing the recovered carbon residue as a conductive agent. The viability of recycled carbon residue as a conductive agent for

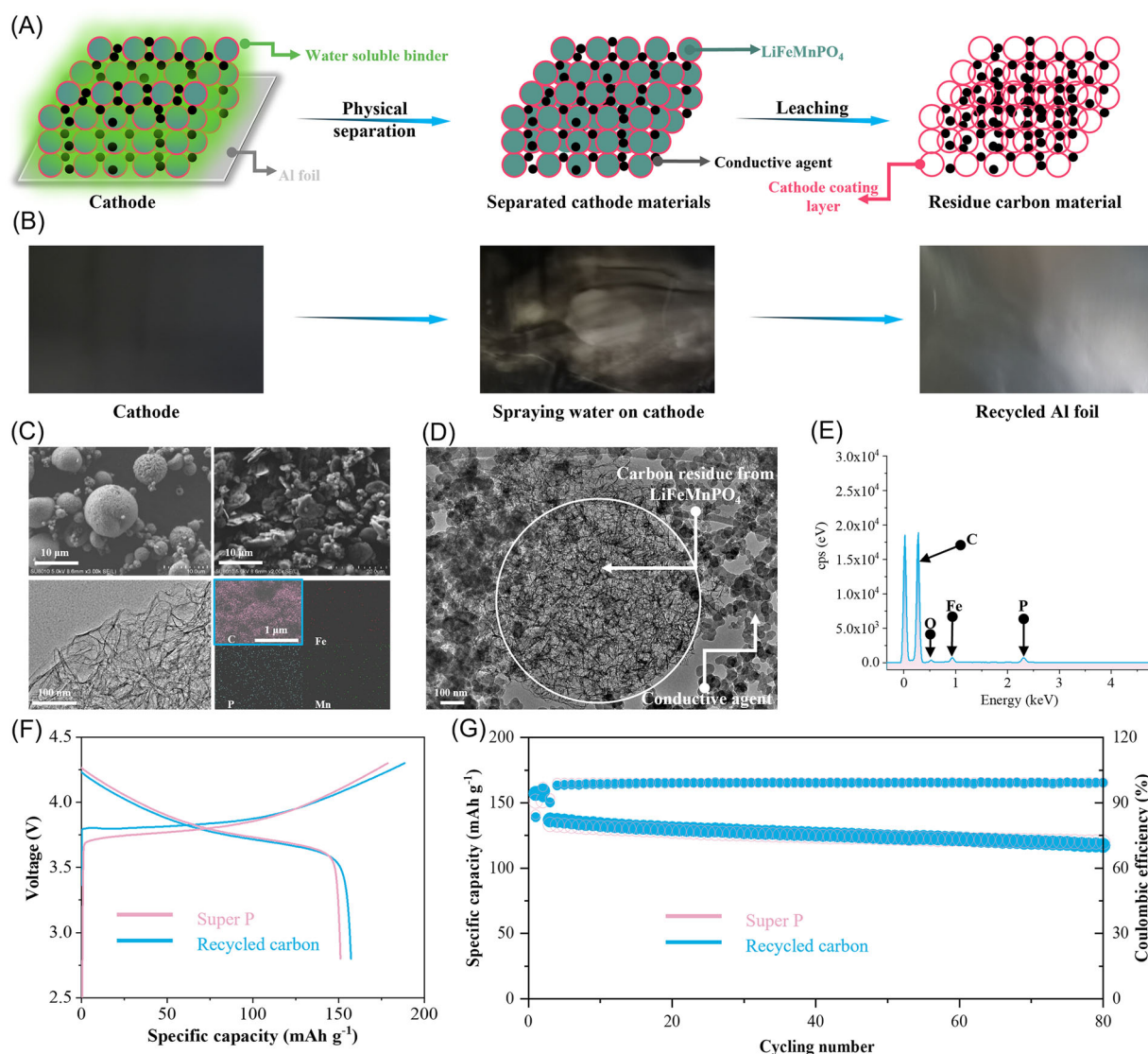


FIGURE 3 (A) A concept design for an easily recycled LiFeMnPO₄-based cathode and the associated recycling process. (B) The optical images of the separation of the LiFeMnPO₄-based cathode with a polyacrylic acid binder. (C) The electron micrographs of LiFeMnPO₄ particles and graphene recovered from their conductive coating. (D) The TEM image of recycled carbon residue from a LiFeMnPO₄ cathode, and (E) the corresponding EDX profile. (F) The voltage and capacity curves of NMC333 half cells with super P and recycled carbon residue as conductive agents. (G) The cycling performance of NMC333 half cells with super P and recycled carbon residue as conductive agents.

LIBs was assessed by assembled NMC333 half cells. Figure 3F shows that these NMC333 cells had an initial specific capacity of 188 mAh/g with a Coulombic efficiency of 83.5%. For comparative purposes, commercial NMC333 half cells had a slightly lower specific capacity of 179 mAh/g and a negligible higher initial CE of 84.8%. The minor differences in NMC333 cells may be due to the increased oxygen content of the carbon residues. Cycling performance reveals that the recycled carbon showed similar stability to super P: NMC333 half cells made using recycled carbon, and super P retained 86.7% and 88.3% of their stable capacity after 80 cycles, respectively (Figure 3G).

2.3 | Environmental and economic analysis

Their recycling was analyzed quantitatively to illustrate the advantages of LiFeMnPO₄-based cathodes over traditional methodologies. Recycling efficiencies nearing full recovery were achieved for the active cathode material, conductive agent, and Al foil. In contrast, conventional pyrometallurgical, hydrometallurgical, and direct physical recycling methods have recovered active cathode materials and Al foil with many impurities and below 90% recycling efficiency.¹⁹ The conductive agents account for 1%–2% of the mass of LIBs and 3% of the overall cost (Tables S2 and S3).

Pyrolysis of the conductive agent in spent LIBs is predicted to increase greenhouse gas emissions by 10% during recycling. Thus, pyrolysis of the conductive agent has no economic benefit and is a potential source of environmental pollutants. The LiFeMnPO_4 -based cathode with water-soluble binder design outlined here significantly reduces material and energy consumption during the cathode separation process. The leaching of the active cathode material is feasible without oxidants or heating compared to other cathodic materials utilizing PVDF binders. This reduces the material and energy consumption required for recycling by 20% and 7%, respectively. This method reduces CO_2 emission by $\sim 11.1\%$, or 162 g per kg of material, compared to traditional hydrometallurgical methods (Table S4).

In comparison, the economic value of recycling LiFePO_4 and $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ cathodes are comparable due to the low valuation of metal elements. The precise separation of the easily disassembled cathode can significantly improve recycling profitability. For instance, with precise separation, the profitability of $\$3231.9 + 10.59x$ ($0 < x < 1$) ($22160.9 + 72.62x$ ($0 < x < 1$) CNY) can be achieved for 1 tonne of degraded $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ cathode, with $\sim \$133$ (918 CNY) per kg of cathode revenue from conductive agent recycling (Table S5). Therefore, bringing in recycle-oriented designs for cathodes could dramatically improve recycling efficiency, reduce environmental impact, and increase the profitability of LIB recycling.

2.4 | LiFeMnPO_4 /graphite LIBs with PAA and carbon paper

Separation of the battery from the materials is ultimately a matter of separating the current collector, active materials, conductive agent, and binder. A readily soluble binder facilitates the separation of the current collector and subsequent materials. These electrode separation processes are designed to ensure that the current collector does not mix with other materials. Otherwise, the recycled materials require further purification. Metals, including copper and aluminum foils, are a potential source of contaminants that have caused significant problems during recycling. Unfortunately, the copper and aluminum foils are fragile and are readily incorporated into recyclable materials. Aluminum foil is also prone to oxidation and corrosion, which increases the potential for contamination of recycled materials. As a result, it remains challenging to ensure that the metal content of the recycled materials is below two parts per million.

One approach to avoid potential metal contamination is to substitute metal for carbon paper in the current collector so the recovered materials from LIBs lack metal impurities, making them more suitable for subsequent reuse. As shown in Figure 4, the discharged LIBs can be disassembled into shell, separator, cathode, and anode (Figure 4A–E). From the disassembled cathode and anode, the current collector and active materials/

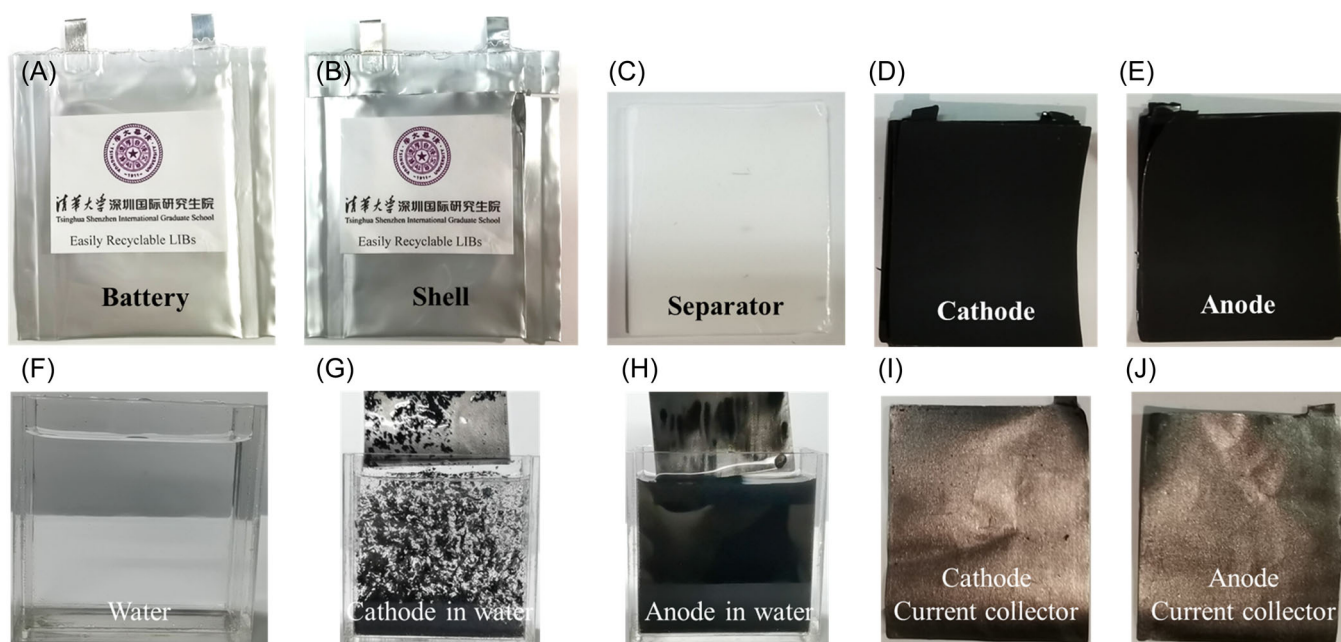


FIGURE 4 (A) The LiFeMnPO_4 /graphite LIB with PAA and carbon paper. Disassembled (B) shell, (C) separator, (D) cathode, and (E) anode. (F) The water tank. (G) The cathode in water. (H) The anode in water. (I) Separated current collector from the cathode. (J) Separated current collector from the anode.

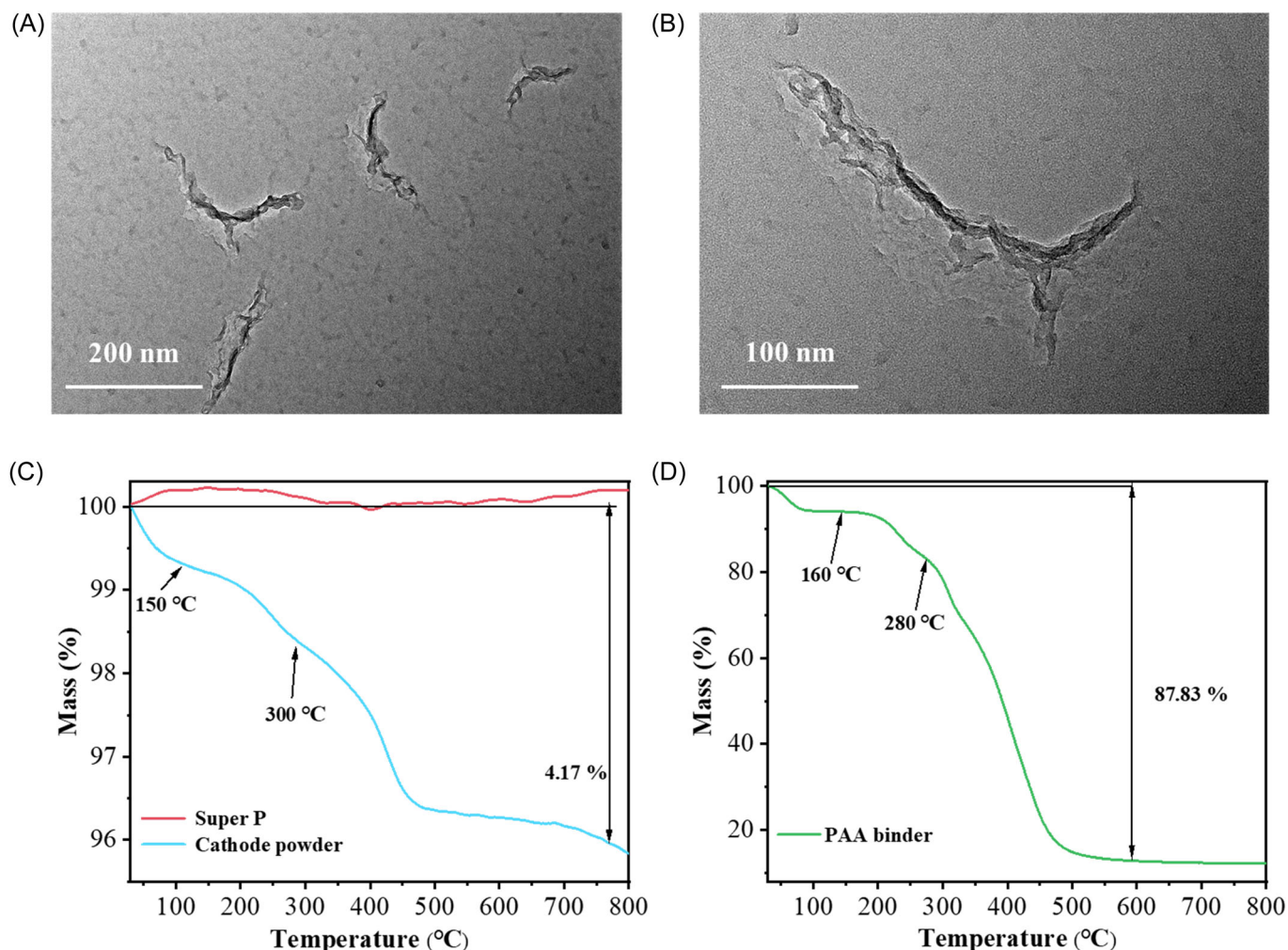


FIGURE 5 (A, B) The transmission electron microscopy (TEM) images of residual PAA in recovered cathode materials. (C) The thermogravimetric analysis (TGA) curves of super P and recovered cathode materials. (D) the TGA curve of PAA binder.

conductive agent can be separated very easily by simply immersing them in water (Figure 4F–J). Even if the separated cathode materials contain carbon, impurities can be removed directly by heat treatment or physical methods.

2.5 | Limitation of the soluble binder

The water-soluble binder PAA allows for the separation of the cathode material and the current collector. However, the PAA binder in the material cannot be completely dissolved in water. Figure 5A,B show the PAA detection in the recovered cathode materials after multiple water washes and ultrasonic treatment. Figure 5C shows that the recycled cathode material decomposes by 4.17% before 800 °C in an Ar atmosphere, which agrees with the decomposition of PAA (Figure 5D). The TGA decomposition of PAA leads to

the mass percentage of 12.17 carbon materials, indicating that only a fraction of PAA (~5%) in the recycled cathode materials is dissolved in water. This could be due to the strong interaction between the binder, active materials, and conductive agent, possibly forming irreversible chemical bonds. Fortunately, the decomposition of PAA increases the carbon content in the conductive agent by 11.56%, which does not significantly change the conductive agent's properties. Therefore, extensive research is still required to select suitable binders and processing methods for efficiently developing recyclable LIBs.

3 | CONCLUSIONS

This research represents a proof-of-concept for the design of an easily recyclable LIB cathode using LiFeMnPO_4 as the active cathode material and a water-soluble PAA binder. The cathode is easily separated into its

constituent materials, recovered in high-purity form, and suitable for reuse, which could significantly improve the circularity of the LIB industry. The water-soluble binder allows for the separation of the Al foil current collector from the cathode materials by a simple water wash. The separated cathode can be leached with acid extraction that separates the active materials from the residual carbon, resulting in a high-purity carbon material that can be reused as a conductive agent without significantly impacting performance. The methodology could benefit recycling manufacturing scraps, which account for 5%–10% of the wasted materials in spent LIBs.

Due to environmental concerns associated with the use of PVDF, environmentally friendly and water-soluble binders are being developed for use in LIBs. Water-soluble binders have already been successfully used in the anode materials in LIBs, resulting in nearly 100% recycling of copper foil, graphite, and conductive agents. If the same approach is applied to cathode materials, the recycling of LIBs could be significantly simplified. Future research focusing on developing soluble cathode materials and binders with collaboration between researchers and battery manufacturers is fundamental to the next generation of LIBs to achieve LIBs with high performance oriented toward recyclability. Ensuring a circular economy for the LIB industry is critical for securing energy security, managing resource consumption, and delaying the natural depletion of lithium reserves.

ACKNOWLEDGMENTS

This research was financially supported by the Key-Area Research and Development Program of Guangdong Province (No. 2020B090919003), National Natural Science Foundation of China (No. 52261160384 and 52072208), Fundamental Research Project of Shenzhen (No. JCYJ20220818101004009), Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01N111), Guangdong Basic and Applied Basic Research Foundation (No. 2022A1515110531), Shenzhen Science and Technology Program (KCXFZ20211020163810015), and China Postdoctoral Science Foundation (No. 2022M721800). The authors acknowledge the support of the Testing Technology Center of Materials and Devices of Tsinghua Shenzhen International Graduate School (SIGS) and the Major Science and Technology Infrastructure Project of Material Genome Big-science Facilities Platform supported by the Municipal Development and Reform Commission of Shenzhen.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Yun Zhao  <http://orcid.org/0000-0001-6003-3136>

REFERENCES

1. Mao J, Ye C, Zhang S, et al. Toward practical lithium-ion battery recycling: adding value, tackling circularity and recycling-oriented design. *Energy Environ Sci.* 2022;15:2732-2752.
2. Zhao Y, Kang Y, Fan M, et al. Precise separation of spent lithium-ion cells in water without discharging for recycling. *Energy Storage Mater.* 2022;45:1092-1099.
3. Zhang R, Meng Z, Ma X, et al. Understanding fundamental effects of Cu impurity in different forms for recovered $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials. *Nano Energy.* 2020; 78:105214.
4. He Y, Yuan X, Zhang G, et al. A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries. *Sci Total Environ.* 2021;766:142382.
5. Zhao Y, Fang LZ, Kang YQ, et al. A novel three-step approach to separate cathode components for lithium-ion battery recycling. *Rare Met.* 2021;40:1431-1436.
6. Fan MC, Zhao Y, Kang YQ, et al. Room-temperature extraction of individual elements from charged spent LiFePO_4 batteries. *Rare Met.* 2022;41(5):1595-1604.
7. Fan MC, Wozny J, Gong J, et al. Lithium metal recycling from spent lithium-ion batteries by cathode overcharging process. *Rare Met.* 2022;41(6):1843-1850.
8. Li L, Zhang X, Li M, et al. The recycling of spent lithium-ion batteries: a review of current processes and technologies. *Electrochem Energy Rev.* 2018;1:461-482.
9. Xiong S, Ji J, Ma X. Environmental and economic evaluation of remanufacturing lithium-ion batteries from electric vehicles. *Waste Manag.* 2020;102:579-586.
10. Ji G, Wang J, Liang Z, et al. Direct regeneration of degraded lithium-ion battery cathodes with a multifunctional organic lithium salt. *Nat Commun.* 2023;14(1):584.
11. Wang J, Zhang Q, Sheng J, et al. Direct and green repairing of degraded LiCoO_2 for reuse in lithium-ion batteries. *Natl Sci Rev.* 2022;9(8):nwac097.
12. Nwachukwu IM, Nwanya AC, Ekwealor ABC, Ezema FI. Recent progress in Mn and Fe-rich cathode materials used in Li-ion batteries. *J Energy Storage.* 2022;54:105248.
13. Hu L, Qiu B, Xia Y, et al. Solvothermal synthesis of Fe-doping LiMnPO_4 nanomaterials for Li-ion. *J Power Sources.* 2014;248:246-252.
14. Hu Q, Liao J, Xiao X, et al. Ultrahigh rate capability of manganese based olivine cathodes enabled by interfacial electron transport enhancement. *Nano Energy.* 2022;104: 107895.
15. Liu S, Zheng J, Zhang B, et al. Engineering manganese-rich phospho-olivine cathode materials with exposed crystal {0 1 0} facets for practical Li-ion batteries. *Chem Eng J.* 2023;454:139986.

16. Zhang Z, Zeng T, Qu C, et al. Cycle performance improvement of LiFePO_4 cathode with polyacrylic acid as binder. *Electrochim Acta*. 2012;80:440-444.
17. Lee JH, Kim JS, Kim YC, Zang DS, Paik U. Dispersion properties of aqueous-based LiFePO_4 pastes and their electrochemical performance for lithium batteries. *Ultramicroscopy*. 2008;108(10):1256-1259.
18. Zhu XH, Li YJ, Gong MQ, et al. Recycling valuable metals from spent lithium-ion batteries using carbothermal shock method. *Angew Chem Int Ed*. 2023;135(15): e202300074.
19. Dai Q, Gaines L, Spangenberg J, Kelly JC, Ahmed S, Wang M. *Everbatt: A closed-loop battery recycling cost and environmental impacts model*. 2019. www.Anl.Gov/egs/everbatt

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Du H, Kang Y, Li C, et al. Easily recyclable lithium-ion batteries: Recycling oriented cathode design using highly soluble LiFeMnPO_4 with a water-soluble binder. *Battery Energy*. 2023;2:20230011. doi:10.1002/bte2.20230011