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Recovery of Graphite from Spent Lithium-Ion Batteries for Use in Conductive Ink Preparation

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ABSTRACT

This study presents a cost-effective and environmentally friendly approach for recovering graphite from spent lithium-ion batteries (LIBs) and reusing it as a precursor for the preparation of flexible conductive inks. Graphite was recovered from the anode through a mechanical separation process, followed by chemical purification using 1 M HCl to remove residual metal ions (Li, Co, Ni), and subsequent thermal treatment at 1000 °C in an inert atmosphere to eliminate organic binders (PVDF) and partially restore the defective crystalline structure caused by charge/discharge cycling. The purified graphite exhibited a high carbon purity (> 93.4 %) and was used to formulate conductive inks with poly(vinyl pyrrolidone) (PVP) as the polymer binder and carbon black (CB) as a conductivity enhancer. The optimal ink composition was determined using the Response Surface Methodology (RSM). The optimized ink showed good electrical conductivity (surface resistance ≈ 415 Ω/cm) and excellent mechanical flexibility, maintaining stable conductivity under a bending radius of 0.5 cm. These results provide a sustainable solution for waste battery management and contribute to the advancement of low-cost printed electronics technology.

Introduction

During the past decade, the rapid growth of consumer electronics and electric vehicles has led to a sharp increase in the number of spent lithium-ion batteries (LIBs). Improper disposal of these batteries poses serious environmental threats and results in the loss of valuable materials [4,8]. Graphite, the primary component of the LIB anode, accounts for approximately 10 ÷ 15 % of the total battery mass and is a high-value material whose production requires intensive energy consumption (up to 3000 °C during graphitization) [2,14]. Therefore, the recovery and reuse of graphite from spent LIBs not only provide an effective waste management strategy but also represent a promising opportunity to produce advanced materials at a lower cost [1,9].

Conductive inks have recently gained increasing attention as they enable the fabrication of lightweight, flexible, and thin electronic devices through low-cost printing technologies. Among various conductive materials, graphite-based inks have emerged as potential candidates due to their excellent stability, affordability, and chemical inertness, compared with metal-based inks (Ag, Cu, Au) [7,9]. This study focuses on two main objectives: (1) Optimization of the extraction and purification process to obtain high-purity graphite with minimal metallic and polymeric

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contaminants (PVDF) and (2) Application of the recycled graphite as a conductive filler in flexible inks using poly(vinyl pyrrolidone) (PVP) as a binder and carbon black (CB) as a conductivity enhancer [3,6].

This study proposes an integrated approach that spans from the recovery of graphite from spent lithium-ion batteries to its direct application as a conductive filler in functional inks, thereby creating added value from waste resources. The purified recycled graphite was demonstrated to form an effective conductive network when combined with carbon black. The application of RSM enabled quantitative optimization of the relationship between formulation parameters and ink properties, offering greater scientific reliability than conventional trial-and-error approaches. The optimized formulation achieves a balance between electrical conductivity and rheological behavior, meeting the requirements of screen-printing technology. These findings contribute to the development of low-cost conductive materials aligned with the principles of circular economy and sustainable manufacturing.

Experimental

Materials

Hydrochloric acid solution (HCl, 1 M), sodium chloride solution (NaCl, 1 M), spent lithium-ion batteries (LIBs) and ethanol solution (3%) were employed as reagents. Polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, K90, China) with a purity of 99% was used as the polymer stabilizer. Black carbon (BC, China) with a purity above 99% and a particle size of 10–80 nm was also utilized.

Methods

Preliminary recovery:

Spent LIBs were completely discharged by immersion in a 1 M NaCl solution for 24÷48 hours. After disassembly, the anodes (graphite coated on copper foil) were vacuum-dried, and the graphite layer was carefully scraped off and ball-milled at 300 rpm for 2 hours to obtain fine graphite powder [5,13].

Chemical purification:

The crude graphite powder was stirred in a 1 M HCl solution (solid–liquid ratio of 100 g/L) for 30 minutes to dissolve metallic impurities such as Li, Co, Ni, and Al. The solid residue was recovered by vacuum filtration and rinsed with deionized water until neutral pH was achieved. This acid treatment effectively removed metallic residues, increasing carbon purity from 71% to 93.4% [9].

Structural restoration by thermal treatment:

The acid-purified graphite was dried and heat-treated in an inert atmosphere at 1000 °C for 3 hours. The high temperature served two main purposes:(1) Complete decomposition and removal of the PVDF binder (which cannot be fully removed below 600 °C); and (2) Partial restoration of the crystalline structure of graphite that had been damaged during battery cycling, improving its electrical conductivity [11,15].

Ink formulation:

The optimized formulation contained 5% PVP and a total solid content of 0.5 g/mL, with a fixed Graphite/Carbon black mass ratio of 7:3 to increase surface area and conductivity [1,9]. Optimization of the process parameters affecting ink viscosity and surface resistance was carried out using the Box–Behnken design and RSM.

Printing process:

The prepared ink was printed onto a PVC (polyvinyl chloride) substrate, followed by drying under controlled conditions before testing [7,17].

Material characterization:

X-ray diffraction (XRD) was used to identify the crystalline structure; scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to analyze morphology and purity; Fourier-transform infrared spectroscopy (FTIR) was employed to detect organic groups and binder residues [2,6].

Ink characterization:

Viscosity, surface resistance, adhesion, and bending durability, were measured in accordance with Vietnamese standards to evaluate printability and electrical stability

Electrochemical characterization:

Cyclic voltammetry (CV) was conducted in 0.01 M potassium ferrocyanide/ferricyanide solution within a potential range of -0.25 to +1.25 V, at a scan rate of 25 mV/s and sensitivity of 2 mA.

Results and discussion

Characterization of Recycled Graphite (r-Graphite)

Chemical Purification Efficiency and Metal Extraction Mechanism

The recovery of graphite from spent LIB anodes presents a significant challenge in terms of achieving high purity. The mechanically separated graphite typically contains residual metallic contaminants from the cathode ($LiCoO_2$) and binder residues (PVDF),

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resulting in an initial carbon purity of only ~71% (EDX data, Fig. 1.a). Acid washing with 1 M HCl effectively dissolves these metal ions through selective leaching.

Hydrogen ions (H^+) in HCl protonate and desorb the adsorbed Li^+, Co^{2+}, and Ni^{2+} ions from the graphite surface, forming soluble metal chlorides ($CoCl_2$, $NiCl_2$, etc.). As a result, carbon purity increased to over 93.4% (EDX data, Fig. 1.b), confirming that most transition metals were removed. This purification step is essential since even trace metallic impurities can significantly increase the electrical resistivity of conductive inks.

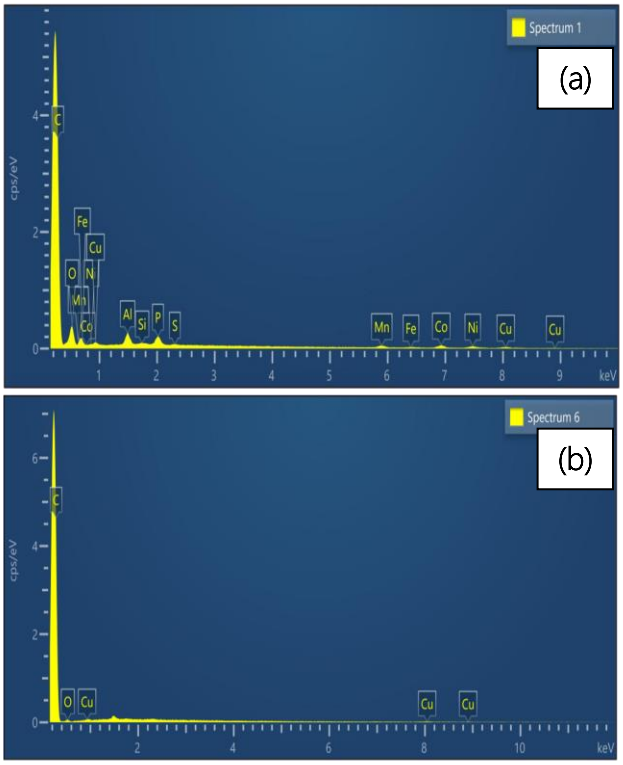

Fig. 1: EDX results of recycled graphite samples from lithium battery anodes before (a) and after (b) treatment with 1M HCl.

This acid leaching process is not merely a simple dissolution but also involves the adsorption/desorption equilibrium of metal ions on the graphite surface. Graphite's hydrophobic nature and low surface area reduce its metal adsorption capacity, allowing HCl to more easily attack and dissolve the adhered metallic particles.

Thermal Treatment for PVDF Removal and Structural Restoration

PVDF (polyvinylidene fluoride) is a thermally stable, nonconductive polymer commonly used as a binder in anodes. If not removed, PVDF forms an insulating layer that disrupts electron transport between graphite particles.

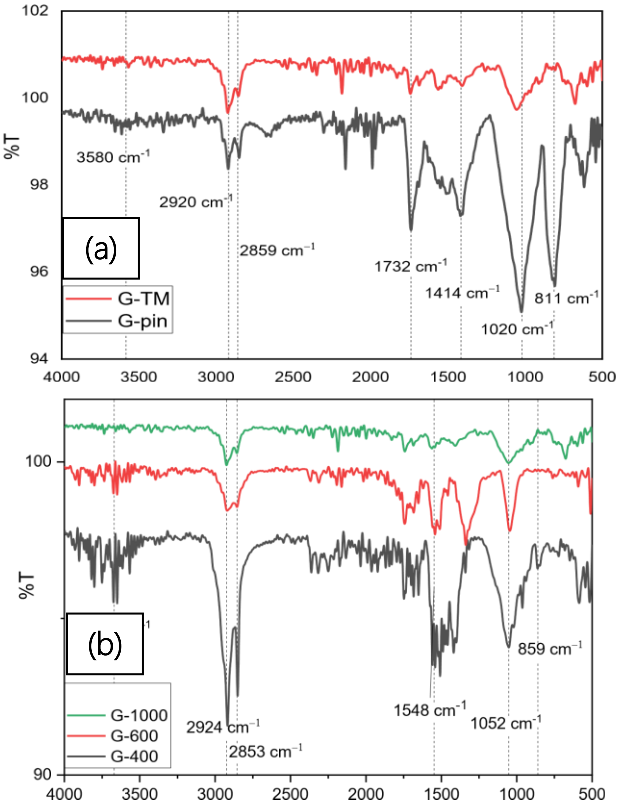

Fig. 2: FTIR results of (a) commercial graphite (red) and graphite recovered from batteries (black) and (b) heat-treated graphite (black: G-400°C, red: G-600°C, and blue: G-1000°C).

FTIR analysis (Fig. 2.a) revealed characteristic absorption bands of both commercial graphite and recovered graphite. Peaks at 3580 cm^{-1} correspond to O–H stretching vibrations from adsorbed water molecules, while peaks near 2920 and 2859 cm^{-1} represent C–H stretching vibrations in the graphite structure. The band at ~811 cm^{-1} is attributed to C–F bonds in PVDF, confirming the presence of binder residues in the recycled sample [6].

After thermal treatment (Fig. 2.b), the FTIR spectra of samples heated at 400 °C, 600 °C, and 1000 °C revealed that the characteristic PVDF peak at 859 cm^{-1} disappeared above 600 °C, indicating complete decomposition of the polymer binder. The process involves pyrolysis, where C–F and C–C bonds in PVDF break down, releasing HF and light hydrocarbon gases. At 1000 °C under inert gas (Ar or N_2), the crystalline structure of graphite was significantly restored.

The XRD results (Fig. 3.a and Fig. 3.b) show that the (002) diffraction peak became sharper and more intense with increasing temperature, indicating higher crystallinity and fewer structural defects. Improved crystallinity correlates directly with enhanced electrical conductivity of the material.

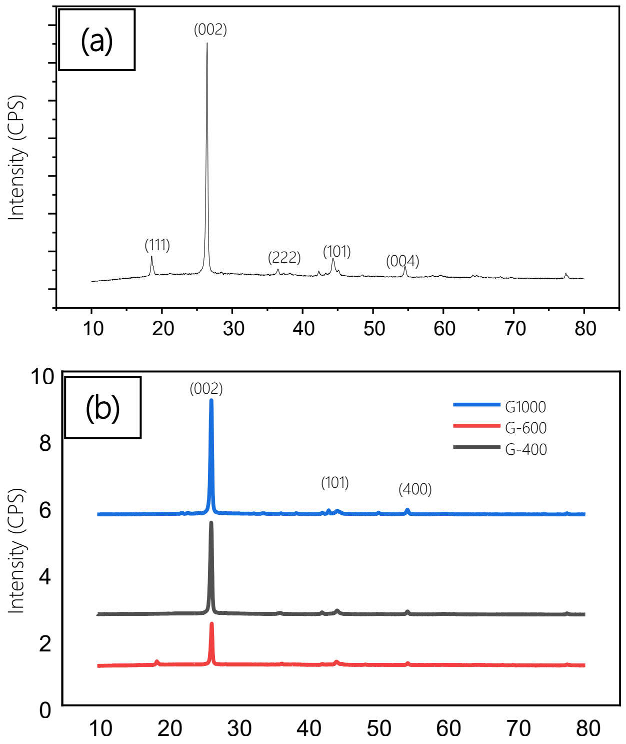

Fig. 3: X-ray diffraction (XRD) results of (a) the graphite sample recovered from the anode and (b) graphite samples treated at 400°C, 600°C, and 1000°C

The XRD results of graphite samples treated at 400°C, 600°C, and 1000°C under an inert atmosphere are presented in Fig. 3.b

Preparation and Optimization of Conductive Ink

Conductive inks must balance electrical conductivity and mechanical adhesion. The recycled graphite (r-Graphite) and carbon black (CB) blend was optimized at a mass ratio of 7:3. The large r-Graphite flakes provide the main conduction pathways, while the nanoscale CB particles fill voids between graphite layers, forming auxiliary conduction networks through the percolation effect. Experimental results demonstrated that the addition of CB reduced surface resistance nearly fivefold (from 2.27 kΩ to 0.5 kΩ), confirming a strong synergistic effect.

Role of PVP: PVP acts as a hydrophilic dispersant and stabilizer. Its carbonyl (C=O) groups adsorb onto graphite and CB surfaces via π–π interactions and hydrogen bonding, preventing particle aggregation and ensuring uniform dispersion. RSM optimization confirmed that a PVP concentration of 5% provided an ideal balance between viscosity, adhesion, and electrical conductivity. The resulting ink achieved a surface resistance of approximately 415 Ω/cm - lower than typical carbon-based inks reported in similar studies. The printed films successfully powered LED lights, confirming their practical conductivity and mechanical robustness.

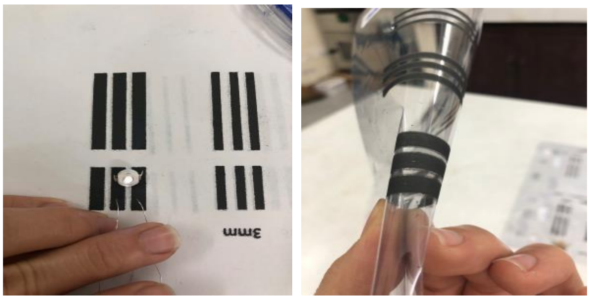

Fig. 4: Electrical conductivity test using an LED and demonstration of flexibility properties.

Bending durability (Fig. 4): The fact that the ink film maintains good electrical conductivity after bending around a 0.5 cm diameter is an important demonstration of the successful combination of [12,17]: (1) the elasticity of the PVP binder and (2) the flexibility of the PVC substrate. PVP acts as an elastic matrix, keeping the r-Graphite and CB particles close together even under mechanical deformation, maintaining the percolated conductive network and preventing complete cracking.

Electrochemical Properties

To investigate the electron-transfer capability of the conductive inks, cyclic voltammetry (CV) measurements were performed on the electrodes in 0.01 M potassium ferro-/ferricyanide solution under the following conditions: potential scan range from 0.25 to 1.25 V; scan rate of 25 mV/s; sensitivity of 2 mA. The resulting CV curves of electrodes printed with commercial graphite ink and recycled graphite ink are presented in Fig. 5.

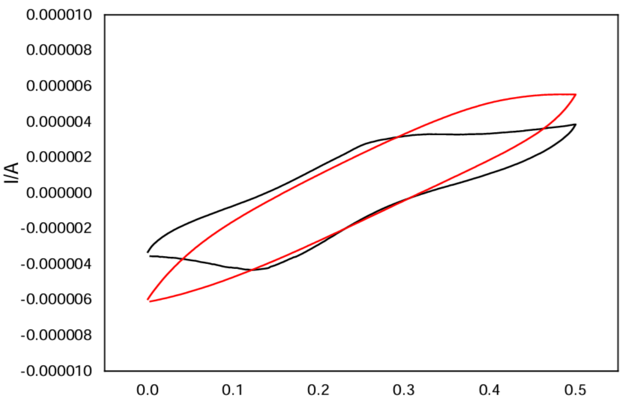

Fig. 5: Polarization curves of the electrodes in 0.01 M potassium ferro-ferricyanide solution (Red: commercial graphite ink; Black: recycled graphite ink).

The r-Graphite electrode exhibited pronounced redox peaks, indicating active electron transfer kinetics, whereas the commercial graphite electrode showed weaker responses. This enhancement can be attributed to the defect-rich surface and edge sites formed during battery cycling and thermal treatment, which serve as electrocatalytically active centers [14,16]. These sites facilitate faster electron exchange and improve redox sensitivity. Thus, the r-Graphite-based ink functions not only as a conductive material but also as an electrochemically active electrode, suggesting promising applications in printed electrochemical and biosensing devices [16].

The optimal ink composition was determined using the Response Surface Methodology (RSM)

The optimal conductive ink formulation derived from recycled graphite was determined using RSM combined with a Box–Behnken experimental design to simultaneously evaluate the effects of three key variables PVP concentration, r-graphite content, and CB content on the electrical resistance and viscosity of the ink.

Optimization was performed using a desirability function approach with the objective of minimizing electrical resistance while maintaining a viscosity suitable for screen-printing applications. The optimal conditions were obtained at a PVP concentration of approximately 3.02%, a r-graphite loading of 0.69 g/mL, and CB content of 0.198 g/mL. Under these conditions, the model predicted a viscosity of about 2000 mPa·s and an electrical resistance of approximately 404 Ω/cm, suggesting an effective balance between conductive network formation and printability. This viscosity range is particularly advantageous for screen printing, as it ensures stable ink transfer through the mesh while preventing excessive spreading after deposition.

Validation experiments yielded a viscosity of 2015 mPa·s and an electrical resistance of 415 Ω/cm, showing good agreement with the predicted values and confirming the reliability and predictive capability of the developed model. The close correlation between experimental and modeled results demonstrates that RSM is a robust tool for guiding material design, significantly reducing experimental effort while maintaining high accuracy.

Overall, RSM not only enabled the precise identification of optimal processing parameters but also provided insight into the structure–property relationships governing the performance of the conductive ink. The optimized formulation exhibits strong potential for applications in printed electronics and functional materials, while also offering a sustainable pathway for the high-value utilization of recycled graphite.

Conclusion

This study demonstrated the technical feasibility and sustainability of recovering and purifying graphite from spent lithium-ion batteries (LIBs). The combined use of acid leaching with 1 M HCl and high-temperature thermal treatment effectively removed metallic impurities and polymeric binders (PVDF), while partially restoring the crystalline structure of graphite. Conductive inks prepared using the recycled graphite, carbon black, and 5% PVP binder exhibited excellent performance, achieving a surface resistance of approximately 415 Ω/cm and maintaining stable conductivity under bending stress. Moreover, the inks showed notable electrochemical activity, suggesting potential use as printed electrode materials for flexible and low-cost electronic and sensing applications.

Although the electrical conductivity remains lower than that of metal nanoparticle-based inks, the results establish a promising foundation for the development of low-cost, carbon-based conductive inks that align with circular economy and sustainable development strategies in the battery recycling and printed electronics industries

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References

1. M. Abdollahifar, S.S. Huang, Y.H. Lin, Y.C. Lin, B.Y. Jheng, M.H. Tu, Y.S. Wu, N.L. Wu, Adv. Mater. Technol., 8(2) (2023) 2200368. https://doi.org/10.1002/admt.202200368
2. N. Cao, Y.L. Zhang, L.L. Chen, J. Power Sources, 483 (2021) 229163. https://doi.org/10.1016/j.jpowsour.2020.229163
3. T.C. de Oliveira Cândido, A.C. Pereira, D.N. da Silva, Analytica, 4(4) (2023) 513-526. https://doi.org/10.3390/analytica4040035
4. E. Fan, L. Li, Z. Wang, J. Lin, Y. Huang, Y. Yao, R. Chen, F. Wu, Chem. Rev., 120(14) (2020) 7020-7063. https://doi.org/10.1021/acs.chemrev.9b00535
5. Y. Gao, C. Zhu, T. Chen, X. Yan, M. Chen, S. Cao, W. Hu, D. Xu, ACS Sustainable Chem. Eng., 8(25) (2020) 9444-9455. https://doi.org/10.1021/acssuschemeng.0c02321
6. Y.Z.N. Htwe, M. Mariatti, J. Taiwan Inst. Chem. Eng., 125 (2021) 402-412. https://doi.org/10.1016/j.jtice.2021.06.022
7. D.S. Kim, J.M. Jeong, H.J. Park, Nano-Micro Lett., 13 (2021) 87. https://doi.org/10.1007/s40820-021-00617-3

8. M. Lehmann, C.G. Kolb, F. Klinger, M.F. Zäh, Mater. Des., 207 (2021) 109871. https://doi.org/10.1016/j.matdes.2021.109871
9. F. Liu, S. Ni, C. Shen, X. Chen, J. Peng, D. Fu, J. Xu, Prog. Org. Coat., 133 (2019) 125-130. https://doi.org/10.1016/j.porgcoat.2019.04.043
10. J. Liu, H. Shi, X. Hu, Sci. Total Environ., 816 (2022) 151621. https://doi.org/10.1016/j.scitotenv.2021.151621
11. M. Shi, G. Wang, C. Sun, J. Yang, S. Liu, T. Fang, C. Xu, Q. Zhu, Fuel, 292 (2021) 120250. https://doi.org/10.1016/j.fuel.2021.120250
12. T.S. Tran, N.K. Dutta, N.R. Choudhury, Adv. Colloid Interface Sci., 261 (2018) 41-61. https://doi.org/10.1016/j.cis.2018.10.010
13. S.D. Widijatmoko, G. Fu, Z. Wang, P. Hall, Sustainable Mater. Technol., 23 (2020) e00134. https://doi.org/10.1016/j.susmat.2019.e00134
14. Y. Yang, X. Meng, Z. Cao, W. Lin, Y. Liu, Y. Sun, Y. Pu, J. Zhan, J. Fang, J. Zhang, Waste Manage., 85 (2019) 529-537. https://doi.org/10.1016/j.wasman.2019.01.008
15. C. Yi, K. Yang, S. Cheng, J. Zhang, L. He, J. Hu, J. Cleaner Prod., 277 (2020) 123585. https://doi.org/10.1016/j.jclepro.2020.123585
16. B. Zhang, Y. Xu, D.S. Silvester, C.E. Banks, L. Ji, H. Gong, J. Power Sources, 589 (2024) 233728. https://doi.org/10.1016/j.jpowsour.2023.233728
17. Y. Zhang, Y. Zhu, S. Zheng, Z.S. Wu, J. Energy Chem., 63 (2021) 498-513. https://doi.org/10.1016/j.jechem.2021.08.011