Proceedings of the Annual General Donald R. Keith Memorial Conference
West Point, New York, USA
April 24, 2025
A Regional Conference of the Society for Industrial and Systems Engineering

Process Evaluation for Graphite Recycling from Spent Lithium-ion Batteries

Abel Alex, Erin Block, Lily Casey, Azan Iftikhar, Emelia Lemza, Kaitlyn O'Dell, Yihao Shen, Xiaotu Ma, Yong Wang, and Yuxin Wang

School of Systems Science and Industrial Engineering, Binghamton University, Binghamton, New York 13902

Corresponding author's Email: eblock2@binghamton.edu

Author Note: All students are graduating seniors at Binghamton University. Their advisor is Dr. Xiaotu Ma, an assistant professor at Binghamton University. The project mentors are Dr. Yuxin Wang and Dr. Yong Wang. The students would like to acknowledge PhD student Yihao Shen and the Analytical & Diagnostics Laboratory at the University.

Abstract: This paper presents a novel experiment that proves the feasibility of using recycled graphite from lithium-ion batteries as a sustainable and effective alternative in battery applications and demonstrates recycled graphite's ability to support a closed-loop battery economy, reducing reliance on virgin materials. In this regard, an experimental procedure was designed and executed to purify graphite anode material from end-of-life lithium-ion batteries. Electrochemical performance comparisons were made between batteries of commercial, spent, and purified graphite yielding results that support the hypothesis. The purification process helps increase electrochemical performance of recycled batteries, nearing commercial standards.

Keywords: Lithium-ion Battery Recycling, Design of Experiments, Graphite Purification

1. Introduction

An increased dependence on renewable energy sources is forming due to the depletion of fossil fuels and a change in lifestyle among people. If not recycled, Lithium-ion batteries will be hazardous to the environment and valuable materials will be discarded. If a battery ends up in a landfill, it can release heavy metals and other toxins that leak into the soil and groundwater. Approximately 5% of lithium-ion batteries are recycled globally, and if this number remains the same, the total global battery waste will reach 8 million tons by 2040 (Baum, 2021). Not only are there significant environmental impacts resulting in the need for recycling, but limited resources of metals are also a motivator. China is responsible for 99% of the world's supply of rare metals, including graphite, an essential component in lithium-ion batteries. The country has banned these exports, leaving the US with very little graphite supply, as there are no domestic mining operations (Baskaran, 2024). Recycling graphite from batteries results in an almost infinitely reusable and low cost alternative to importing graphite.

A sustainable, scalable method for recovering high-purity graphite from lithium-ion battery black mass is using mild pyrolysis and acid leaching. This method provides a high graphite recovery rate, offering an affordable, circular alternative to virgin graphite for battery anodes (Wei et al., 2024). The streamlined, energy-efficient method for recovering graphite from lithium-ion battery black mass using pyrolysis and leaching shows great results when examining through various electrochemical tests. The recovered graphite, especially from EV batteries, demonstrated superior purity and performance, supporting direct reuse in LIB anodes and advancing circular economy goals (Chernyaev et al., 2024).

2. Methodologies

A Design of Experiments was developed and performed to prove the feasibility of recycling and reusing graphite from spent lithium-ion batteries. Methods within the Design of Experiments are adopted from previous studies. The hypothesis being tested is that purified graphite can perform sufficiently compared to commercial graphite. The four overarching steps are 1) assembly of commercial and spent graphite batteries, 2) purification of spent graphite and assembly of purified graphite batteries, 3) graphite characterization, and 4) electrochemical testing. These steps encompass the full scope of the experiment with the purification process as the focus, where the spent graphite undergoes a chemical process to improve its performance. Spent graphite is a material that comes from used batteries and is known to have many impurities during battery usage and the recycling process.

The first step of the experiment is creating and assembling batteries using spent and commercial graphite. Using graphite samples, slurries are created containing the specific graphite, polyvinylidene fluoride (PVDF) binder, carbon, and Nmethyl-2-pyrrolidone (NMP) in an 8:1:1 ratio (Displayed in Table 1 below) respectively with the NMP being adjusted as needed. The components are mixed at 2,000 RPM for 4 minutes. Once combined, the slurry is cast uniformly over a copper foil substrate, left to dry for 12 hours at 80 degrees Celsius, then put through a roller press to ensure adhesion. The foil is cut into circular dies with a 15mm diameter, which are the graphite electrodes. The amount of active material, graphite, is calculated for use in future steps. The graphite electrodes are then assembled into half cell batteries. The order of assembly is displayed in Figure 1. A separator, spacer, lithium metal sheet, polymer separator, graphite electrode, two separate applications of 90 mL of LP30 are all crimped in between metal casings. The same steps were followed to create both commercial and spent graphite batteries.

Table 1. Black Slurry Composition Per Graphite Type

	Commercial	Purified	Ratio
AAM	0.16 g	0.40 g	8
CB	0.02 g	0.05 g	1
PVDF	0.02 g	0.05 g	1
NMP	0.43 mL	0.90 mL	-

The second step is to purify graphite and assemble the purified graphite batteries. Spent graphite is rinsed with 30% sulfuric acid solution that has a concentration of 5 mol/L. The acid is stirred with the graphite for 30 minutes at room temperature. Once the stir cycle is completed, it is rinsed with water and filtered with a pump, and then the resulting purified graphite powder is placed in an oven to extract the remaining liquid and fully dry. The purified graphite is then put through the same methods for electrode casting and battery assembly as the other battery types, resulting in batteries made from purified graphite.

The third step is graphite characterization, where Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) are used to collect initial data on all graphite types: purified, commercial, and spent. SEM is a technique that uses focused beams of electrons and a microscope to produce high resolution images of a sample, providing information on its topography and morphology. SEM analysis is performed on samples of commercial graphite used in the manufacturing of Li-ion batteries and spent graphite from end-of-life batteries. The goal is to examine the surface structure of these samples and compare them to purified graphite samples. XRD is a technique used to determine the crystal structure of a sample, identifying its chemical composition and impurities (Ural, 2021). In the test itself, X-ray beams are directed towards a sample which in return creates interference at various angles. According to the material, the intensity of beams refracted are recorded at higher frequencies, which then can be compared against a standard reference to confirm composition of the material test. These techniques show the shape and composition of all the graphite types, so it is used to determine if the purification process was a success, and how the graphite types compare in terms of purity and structure.

The final step is electrochemical testing, where all the batteries are put through a series of standard battery tests, including a cyclic voltammetry, impedance, discharge capability, and coulombic efficiency test. The sets of data are used as references to compare the final batteries after the purification process. The final process of the experiment is the comparison of the data results. Images from SEM, graphs from XRD, and data from electrochemical tests are scanned carefully to prove the hypothesis that purified graphite can perform better than spent, and at the level of commercial graphite.

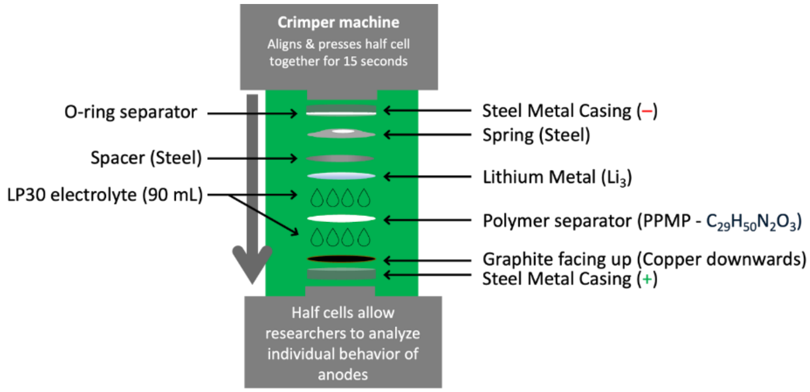


Figure 1. Components of Half Cell Batteries and Order of Assembly (Bottom-Up)

3. Results

3.1 Scanning Electron Microscopy

As part of the characterization of the commercial, spent, and purified graphite, Scanning Electron Microscopy images are captured of each sample. Visual analysis is conducted to understand how the structure of graphite particles may degrade throughout the usage of a battery, and how a purification process can help rebuild the structure. The images reveal that the spent graphite particles exhibit significant surface roughness and fractures compared to the commercial graphite, likely due to battery cycling and degradation. The graphite layers appear separated, suggesting the graphite has become structurally unstable over time. The purified graphite shows improvements in the amount of fractures present, suggesting that the acid process may have improved its structure. However, to achieve more concrete results regarding the success of the purification process, additional testing is conducted to numerically analyze the electrochemical performance of batteries of each graphite type.

3.2 X-Ray Diffraction

The graphs below display XRD test conducted for commercial anode graphite, spent anode graphite and 5 Mol purified spent graphite.

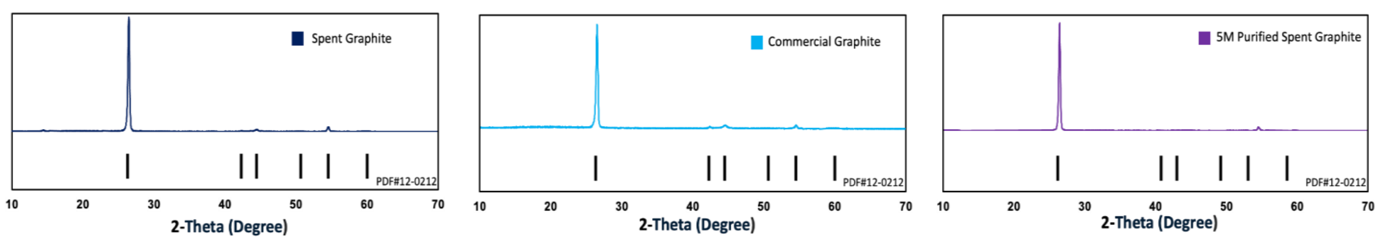


Figure 2: XRD for Commercial, Spent and 5 mol/L Purified Graphite.

All XRD graphs display a constructive interference intensity spike at 26°, and minor spike at 54°, indicating all samples contained graphite. However, the spent graphite results have multiple impurities causing intensity spikes throughout its results. The 5 mol/L spent graphite had the most linear results when compared with commercial and spent XRD results.

Such results propose that following the purification process impurities were removed from the sample providing it with cleaner and purer graphite. To further support these findings, a single factor analysis of variance statistical test was conducted amongst the intensity levels of the three respective samples. The null hypothesis is that the XRD values are the same for all 3 samples, while alternative hypothesis is that they're different.

Table 2. Single factor ANOVA for XRD results

Summary for samples

Groups	*Count*	*Sum*	*Average*	*Variance*
Intensity of Spent graphite	3,000	224,618	74.87	190,012.42
Intensity of Commerical Graphite	3,000	154,431	51.48	32,428.70
Intensity of 5M purified Spent Graphite	3,000	532,514	177.50	2,348,783.47

ANOVA

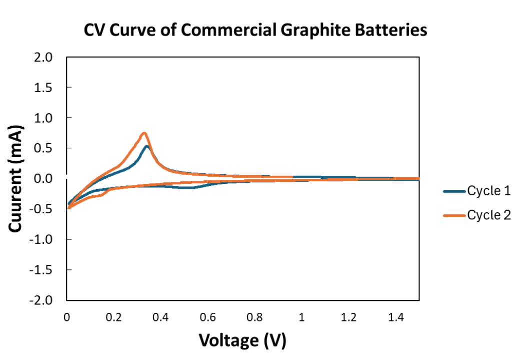
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	26,963,657.41	2	13,481,828.70	15.73	0.0000002	3.00
Within Groups	7,711,102,571.71	8,997	857,074.87			
Total	7,738,066,229.11	8,999				

The ANOVA test findings displayed a P-value of 0.0000002, which is notably less than the threshold value of 0.05. Such results reject the null hypothesis, suggesting a significant difference in XRD results. Spent graphite washed in 5 mol/L sulfuric acid produced purified graphite with a significant difference.

3.3 Cyclic Voltammetry Test

Cyclic Voltammetry (CV) tests are performed on all assembled coin cells to evaluate electrochemical behavior. The voltage is cyclically scanned within a defined window to observe the redox peaks, reaction kinetics and stability over multiple cycles. The CV curves below provide insights into the electrochemical reversibility and potential degradation of the spent and commercial batteries created. The commercial graphite CV curves show clear and well-defined peaks, which means the redox reactions are happening predictably and efficiently. There are also minimal shifts between cycles 1 and 2, indicating good electrochemical stability and low degradation after cycling. The spent graphite CV curves show broader and less distinct peaks, which show reduced reversibility and possibly slower kinetics due to structural damage or impurities. There are also larger shifts between cycles signaling instability.

In terms of performance, commercial graphite behaves as expected with good capacity retention and stable reaction kinetics. Spent graphite, without purification, shows signs of wear such as reduced reactivity, possible side reactions, and poor reversibility. These results support the hypothesis that spent graphite needs purification to restore its performance, as it currently underperforms in electrochemical tests compared to commercial graphite.



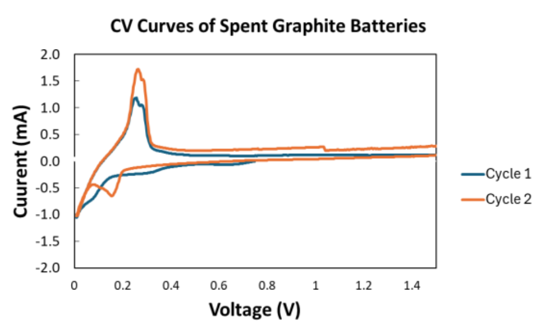


Figure 3: Commercial and Spent Graphite CV Curves for Cycle 1 and 2 of Commercial and Spent Batteries

3.4 Impedance Test

To comprehend the electrical response of a system, an impedance test is carried out. Once tests are finished, data is provided of resistive components (Re(Z)) and inductive components (Im(Z)). Through these variables, a Nyquist plot is created which helps visualize resistance and ion diffusion. From an overall perspective, this provides insight into electrolyte resistance and charge transfer resistance. The focus of the Nyquist graph is the semi circles that form. The larger circle of the spent graphite suggests that purification is needed to better fit the standards shown from commercial graphite.

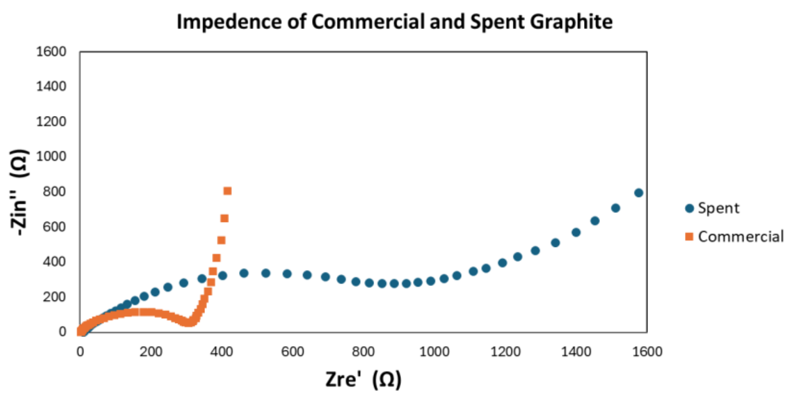


Figure 4: Impedance Test for Commercial and Spent Graphite Batteries

3.5 Discharge Capability

The initial charge and discharge cycle performance of a battery, particularly lithium-ion batteries, significantly impacts its overall lifespan and performance. The first few charge/discharge cycles are crucial for establishing the battery's Solid Electrolyte Interphase formation, which affects the battery's ability to store energy. The coulombic efficiency is the ratio of charge and discharge capacity, indicating better reversibility of graphite. The high initial coulombic efficiency demonstrates better reversibility electrochemical performance of graphite. The theoretical capacity of graphite anode is 372 mAh/g, which means the graphite has better performance if its capacity is closer to the theoretical capacity. In Figure 5, spent graphite exhibits a lower capacity and initial coulombic efficiency, indicating its poor electrochemical performance compared to commercial graphite, which is consistent with its CV and Electrical Impedance Spectroscopy (EIS) results.

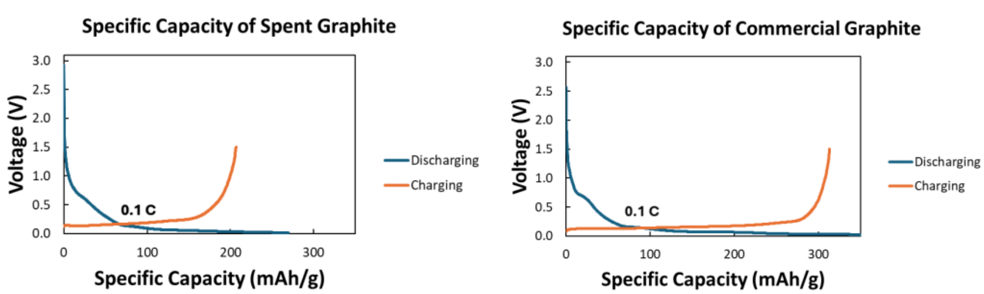


Figure 5: Charge & Discharge Specific Capacity Graphs

3.6 Coulombic Efficiency

A coulombic efficiency analysis indicated that both commercial and spent graphite had good electrochemical reversibility, while cyclic testing demonstrated stable charge-specific capacity performance over several cycles. The number of cycles differs between commercial, 503 cycles, spent, 102 cycles, and purified, 15 cycles for 5M H_2SO_4. Commercial graphite showed the most significant and consistent performance, exhibiting both steady cyclic behavior and the greatest, most stable coulombic efficiency, indicating higher electrochemical stability. The spent graphite takes a few cycles to reach nearly 100% efficiency but still exhibits good stability. The purified samples reached the near 100% efficiency levels slightly quicker than the spent samples, indicating that the purification process improved coulombic efficiency to closer match commercial standards; figure 6 depicts the performance for 3 different cells of commercial, spent, and 5M H_2SO_4 purified cell; which undergoes cyclic testing and obtained improves coulombic efficiency for 5M H_2SO_4.

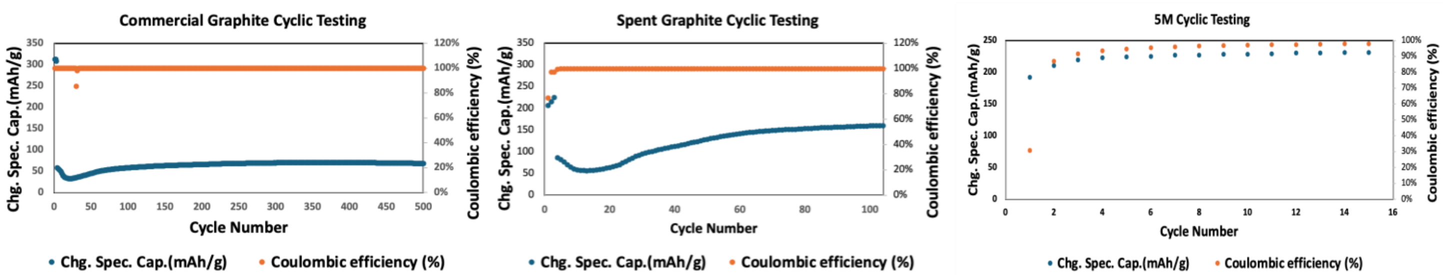


Figure 6: Cyclic Testing vs Coulombic Efficiency

4. Conclusion and Future Work

The above experiment explored the potential to purify and reuse spent graphite from lithium-ion batteries, contributing to sustainability in the energy industry. The electrochemical testing proves that the spent batteries had worse performance than the commercial, suggesting the need for purification. The data collected from the purified batteries shows improvement in coulombic efficiency and therefore does support the hypothesis that purification increases electrochemical performance of recycled batteries. These results are a promising step in the future of sustainability and battery recycling.

To improve the purified graphite process, future work could include using graphene enhancement on the graphite. Graphene has the possibility of creating more electron-conductive pathways and enhancing the structural integrity but also has additional expenses. That trade off could be implemented into an additional experiment and tested.

5. References

Baskaran, G. (2024). What China's Ban on Rare Earths Processing Technology Exports Means. Center for Strategic & International Studies. https://www.csis.org/analysis/what-chinas-ban-rare-earths-processing-technology-exports-means

Baum, Z. (2021, December 21). The next growth wave: lithium-ion battery recycling technologies. Cas.org; CAS. https://www.cas.org/resources/cas-insights/next-growth-wave-lithium-ion-battery-recycling-technologies

Chernyaev, A., Kobets, A., Liivand, K., Tesfaye, F., Hannula, P.-M., Kallio, T., Hupa, L., & Lundström, M. (2024). Graphite recovery from waste Li-ion battery black mass for direct re-use. *Journal of Hazardous Materials, 424*, 127–136.

Ural, N. (2021). The significance of scanning electron microscopy (SEM) analysis on the microstructure of improved clay: An overview. *Open Geosciences*, *13*(1), 197-218.

Wei, X., Guo, Z., Zhao, Y., Sun, Y., Hankin, A., & Titirici, M. (2024, October 30). Recovery of graphite from industrial lithium-ion battery black mass. RSC Sustainability.