Selective recovery of graphite from spent lithium-ion battery black mass using froth flotation

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Abstract. Rapid electric vehicles and electronics growth have driven a sharp rise in Lithium-ion battery (LIBs) production and are expected to increase spent battery waste. The 'black mass' derived from the shredding of spent LIBs is a heterogeneous mixture comprising cathode active materials (lithium cobalt oxide (LCO), nickel-manganese-cobalt oxides (LMCO), lithium iron phosphate (LFP)), anode graphite, current collector foils (aluminum and copper), binders (PVDF), and residual electrolytes and lithium salts. Graphite, a critical anode material in LIBs, has gained prominence as a valuable secondary resource, making its recovery from end-of-life batteries essential for sustainable resource management. Flotation, a proven beneficiation method for natural graphite ores, is now being explored for recovering graphite from secondary sources like spent LIB black mass. This study investigates the selective recovery of graphite from two black mass samples, *BM-1* and *BM-2*, originating from spent LIBs with LFP and LCO chemistries, respectively, through laboratory-scale froth flotation tests using customized collector and frother, namely collector 'C' and frother 'F', which are synthetic, organic, and proprietary reagents. Collector 'C' was varied between 100–500µL, while frother 'F' was varied between 10–50µL to evaluate their influence on carbon (graphite) recovery and grade. Comparative flotation tests revealed distinct behaviors between the two samples, attributed to their unique physical and chemical characteristics and carbon content. For *BM-1*, flotation under optimal conditions (collector 'C': 100µL; frother 'F': 10µL) achieved a high carbon grade of 87.17% but with modest recovery of 43.44%. Conversely, *BM-2*, under the same conditions, yielded a lower carbon grade of 66.49% but a much higher recovery of 53.98%. This preliminary investigation demonstrates the feasibility of substantial graphite recovery from black mass; however, further studies involving pretreatment or additional cleaning stages could significantly enhance both recovery and grade.

Keywords: Lithium-ion batteries (LIBs); Black mass; Graphite recovery; Froth flotation; Spent battery recycling; Secondary resources.

1. Introduction

The accelerated growth of electric mobility and renewable energy storage has drastically increased the production and consumption of lithium-ion batteries (LIBs) worldwide. With their limited service life, the volume of spent LIBs is projected to surge in the coming decade, creating both environmental challenges and opportunities for secondary resource recovery [1, 2]

Spent LIBs, after mechanical treatment such as shredding and sieving, yield a fine fraction known as “black mass”, composed primarily of cathode active materials (e.g., $LiCoO_2$, $LiNi_xMn_yCo_zO_2$, $LiFePO_4$) and anode graphite, together with binders and residual electrolytes [3,4]. Conventional recycling processes, pyrometallurgy and hydrometallurgy, have mainly focused on the recovery of high-value metals such as Co, Ni, and Li. In these processes, graphite is often overlooked, used merely as a reductant in smelting, or lost in leach residues [2]. Such neglect is concerning as graphite constitutes 15–20% (weight) of a LIB and is classified as a critical raw material by the European Commission due to supply risks and high strategic importance [5]. Its recovery would not only reduce pressure on natural resources but also improve the sustainability and economics of LIB recycling.

Froth flotation, a widely applied mineral processing technique, has emerged as a promising method for selectively separating graphite from lithium metal oxides (LMOs) in black mass. The process exploits the natural hydrophobicity of graphite compared to the hydrophilicity of LMOs, enabling the enrichment of anodic graphite in the froth phase while retaining metal oxides in the tailings [2, 3]. Recent studies have demonstrated that flotation could achieve graphite recoveries of 85–90% with purities exceeding 90% when optimized reagent schemes and pre-treatments are applied [1, 4, 5]. Nevertheless, challenges remain in ensuring efficient separation due to binder residues, electrolyte decomposition products, and the entrainment of ultrafine particles, which can reduce selectivity [4]. Pre-treatment methods such as pyrolysis, attrition conditioning, and sonication have been explored to mitigate these issues and enhance flotation performance [3, 4]. Moreover, the reuse of recovered graphite is under active investigation. While closed-loop recycling for LIB anode reuse, meeting battery-grade purity, remains challenging, open-loop applications, such as those in refractory materials, have shown promising results, broadening the value chain of recovered graphite [5]. Given these considerations, the selective recovery of graphite from spent LIB black mass via froth flotation represents a

crucial step toward improving material efficiency and achieving circular economy goals in the battery industry.

2. Materials and Methods

2.1. Materials

Two black mass samples, designated *BM-1* and *BM-2*, were sourced from a local lithium-ion battery recycling facility in India. *BM-1* is derived from Lithium Iron Phosphate (LFP) battery chemistry, while *BM-2* is from Lithium Cobalt Oxide (LCO) chemistry. These samples represent a heterogeneous mixture of anode (primarily graphite) and cathode materials. *BM-1* contains 55.53% carbon, whereas *BM-2* contains 37.53% carbon.

The flotation experiments were conducted using a customized collector and frother, designated as Collector 'C' and Frother 'F', respectively. Both reagents are proprietary, synthetic organic compounds.

2.2. Flotation Tests

All froth flotation tests were conducted in a Denver D-12 laboratory flotation machine with a 1 L cell. A slurry was prepared by mixing 100 g of black mass with tap water to achieve 10% (w/v) pulp density and then agitated at 900 rpm for 5 minutes. Collector 'C' was tested at 100–500 µL and frother 'F' at 10–50 µL. For each test, the collector was added first and conditioned for 3 minutes, followed by the frother, which was then conditioned for 1 minute. Flotation was then carried out with an air flow at 2 L/min, and the froth was collected for 5 minutes. Both concentrate and tailings were filtered, dried, weighed, and analyzed for carbon content to determine weight recovery, carbon grade, and recovery.

3. Results and Discussion

To evaluate the efficiency of graphite separation from different cathode chemistries, flotation studies were conducted on *BM-1* and *BM-2* black mass samples under varying collector and frother dosages. The performance in terms of mass, carbon grade, and carbon recovery is compared in Fig. 1.

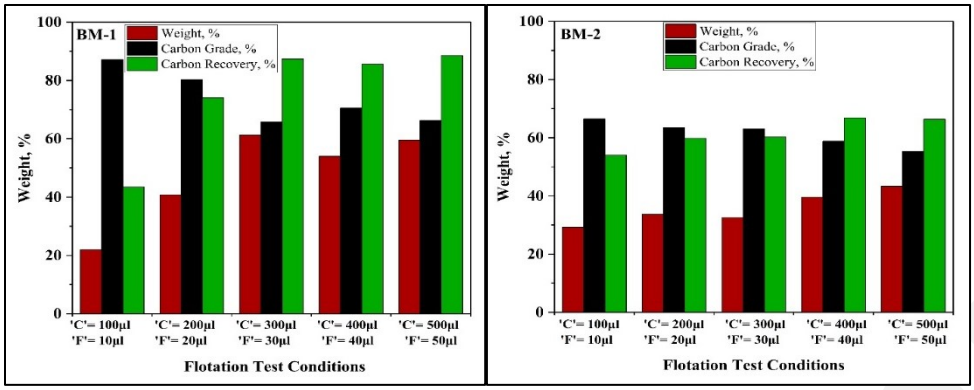

Fig. 1 Comparative flotation performance of *BM-1* and *BM-2* black mass showing weight %, carbon grade, and carbon recovery % in the float product under varying collector ('C') and frother ('F') dosages.

For *BM-1*, the lowest dosages ('C' = 100 µL; 'F' = 10 µL) yield the highest carbon grade (~87%) but modest recovery (~43%), showing good selectivity with limited yield. Increasing reagent levels sharply boost recovery, peaking near 90%, but grade falls to ~63% due to impurity entrainment, with float mass also increasing and diluting carbon purity. For *BM-2*, low dosages give lower grade (~67%) but higher recovery (~54%) than *BM-1*, indicating less selectivity. With higher dosages, recovery rises and weight percentage increases, but grade remains consistently lower. At the highest dosages, recovery levels off near 73%, while the grade drops to ~57%, illustrating the typical grade–recovery trade-off.

4. SEM analysis of flotation products

Scanning Electron Microscopy (SEM) was employed to characterize the morphological differences between the float and non-float products from the flotation study, thereby assessing the efficacy of the separation process (Fig. 2a & 2b).

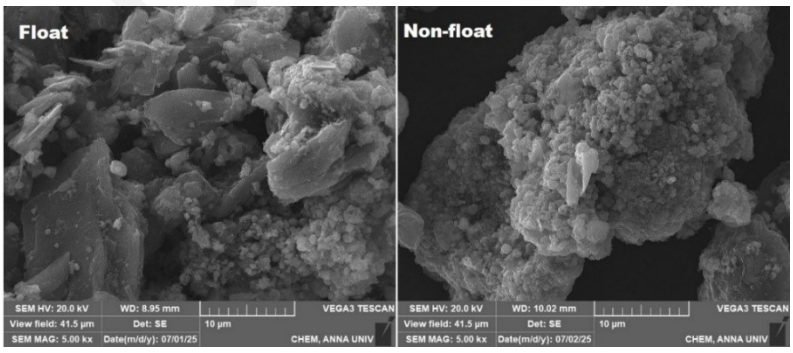

Fig. 2a SEM micrographs of *BM-1* black mass flotation products- float and non-float

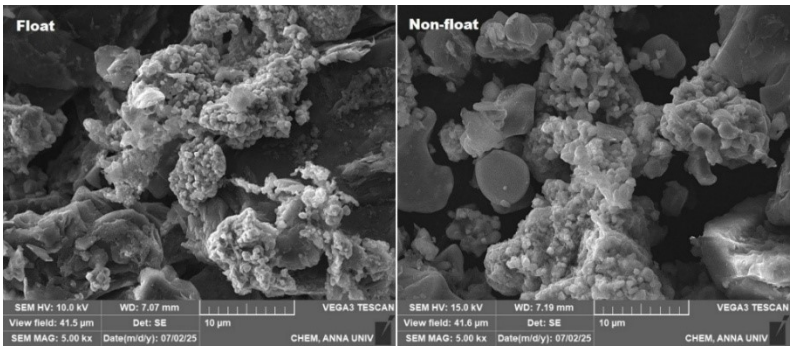

Fig. 2b SEM micrographs of *BM-2* black mass flotation products- float and non-float

SEM imaging confirms the complex nature of both black mass samples, revealing a highly mixed composition of particles with significant variations in shape and size [6]. This morphological complexity is further underscored by the non-smooth, irregular, and bumpy surface texture observed on the particles. Both samples show an agglomeration of particles, may be due to the PVDF binder [7].

For *BM-1* (Fig. 2a), the float product mainly consists of irregularly shaped, plate-like graphite flakes, indicating effective impurity removal and high flotation selectivity. In contrast, the non-float contains irregular, angular particles typical of LFP and other residues, with rough, agglomerated surfaces. The lack of large graphite flakes in the non-float confirms that most graphite was successfully recovered in the float fraction. For *BM-2* (Fig. 2b), the float fraction shows irregularly shaped, platy particles, often referred to as flakes (graphite), indicating efficient separation and carbon enrichment. The non-float contains dense, angular particles with rough, aggregated surfaces typical of $LiCoO_2$ and other oxides, confirming that cathode material dominates this fraction rather than graphite.

5. XRD analysis of float products:

To complement the morphological analysis provided by SEM, X-ray Diffraction (XRD) was performed on the float and non-float products from both the *BM-1* and *BM-2* black mass flotation studies (Fig. 3).

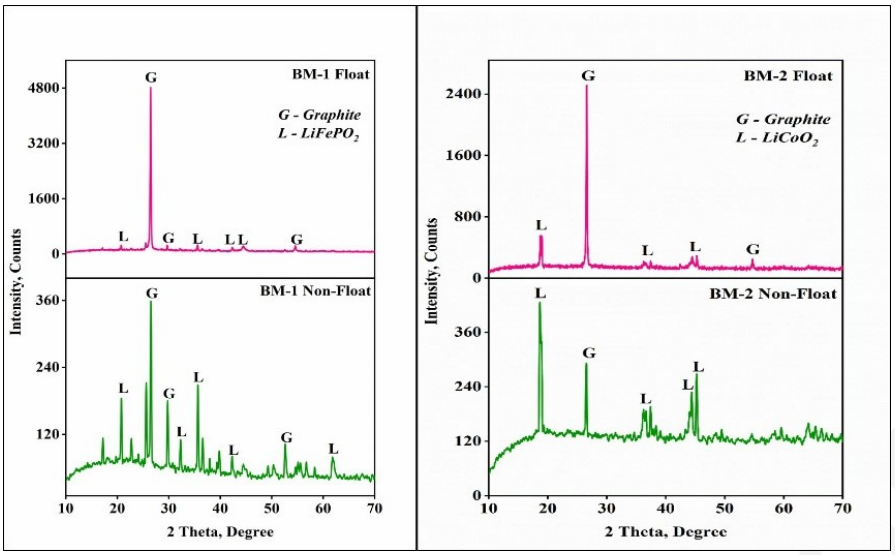

Fig. 3 XRD patterns of the flotation products of *BM-1* and *BM-2* black mass

The XRD patterns of the flotation products provide clear evidence of phase separation between graphite and cathode materials in the spent LIB black mass. In both *BM-1* and *BM-2* samples, the float fraction is dominated by sharp and intense diffraction peaks corresponding to graphite, confirming its successful recovery in the froth product. The non-float fractions show distinct reflections attributed to cathode phases $LiFePO_4$ for *BM-1* (LFP) batteries [8] and $LiCoO_2$ in the case of *BM-2* (LCO) batteries [7], along with minor peaks from associated metal oxides. The relative absence of graphite peaks in the non-float fraction further validates the selectivity of the flotation process.

5. Conclusions

The froth flotation process, under the tested reagent conditions, exhibits a significant difference in separation efficiency between the two types of black mass. The results demonstrate that froth flotation is highly effective for the LFP system (*BM-1*), delivering a clean and selective separation of graphite and cathode material. In contrast, the LCO system (*BM-2*) suffers from poor selectivity, with substantial contamination of the graphite concentrate by cathode particles. Both systems show minor graphite losses to the non-float fraction. Further studies to achieve an effective separation with high-purity graphite require optimized strategies, such as tailored reagents, number of cleanings, selective depressants, or pulp chemistry modifications.

6. References

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