

# Separation of graphite from cathode materials in spent lithium-ion batteries using flotation technology

L Verdugo<sup>1</sup>, A Hoadley<sup>2</sup>, L Zhang<sup>3</sup>, B Etschmann<sup>4</sup>, W Bruckard<sup>5</sup> and J M Menacho<sup>6</sup>

1. PhD Student, Monash University, Melbourne Vic 3800. Email: luis.verdugo@monash.edu
2. Assoc. Professor, Monash University, Melbourne Vic 3800.  
Email: andrew.hoadley@monash.edu
3. Assoc. Professor, Monash University, Melbourne Vic 3800. Email: lian.zhang@monash.edu
4. Research Officer, Monash University, Melbourne Vic 3800.  
Email: barbara.etschmann@monash.edu
5. Research Group Leader, CSIRO, Melbourne Vic 3169. Email: warren.bruckard@csiro.au
6. General Manager, De Re Metallica Ing. SpA, Santiago, Chile, 8581151.  
Email: jorge.menacho@drm.cl

## INTRODUCTION

Since the introduction of Lithium-Ion Batteries (LIBs) in 1991, the market for lithium-ion cells has been driven by the high demand for portable electronic devices and more recently for batteries for the electric car industry. It is expected to grow rapidly to reach 2600 GWh globally by 2030 (US Government, Office of Energy Efficiency and Renewable Energy, 2021). However, there is a desperate need to recycle LIBs to recover valuable cathode materials and graphite. For this reason, several physical and chemical recycling technologies have been proposed to recover these materials from spent batteries. Amongst these, froth flotation technology is a potential cost-effective technology for separation of the graphite fraction from the lithium oxide components due to the natural hydrophobicity of graphite and density difference between graphite and cathode materials (Folayan *et al*, 2021).

In a typical electrochemical unit, the anode (graphite) and cathode materials represent 22 per cent and 31 per cent of the total weight in the battery (Jacoby, 2019). Graphite, with a particle size distribution between 10–20  $\mu\text{m}$ , is fixed on the copper anode surface using an organic binder such as polyvinylidene fluoride (PVDF) (Vuorilehto, 2018). On the cathode unit, the lithium metal oxides with a particle size distribution between 1–17  $\mu\text{m}$  (Zhang *et al*, 2022) are fixed on the aluminium current collector surface also using a similar organic. Untreated, this binder generates problems in the separation of these materials due to agglomeration of cathode materials and graphite. This is illustrated in the following image (Figure 1) taken for a mixed electrode material (fraction minus 38  $\mu\text{m}$ ) using SEM microscopy.

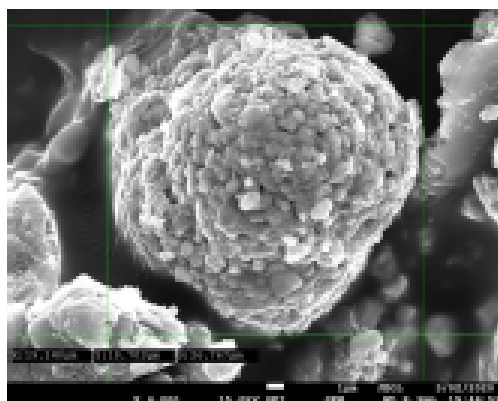


FIG 1 – Electron Micrograph of Agglomeration of Cathode Particles with Organic Binder and Anode Material (image taken by the author of this article).

The importance of the PVDF binder removal is a key aspect in treating the spent battery material. Different pre-treatment techniques such as roasting at high temperature between 500°C–700°C in an inert atmosphere such as nitrogen or argon are known to decompose these organic coatings

(Hanisch *et al.*, 2015). Other techniques include the use of organic solvents such as N-Methyl-2-Pyrrolidone (NMP) or Dimethylformamide (DMF) which dissolve the organic coating thus providing an exposed metal oxide surface (He *et al.*, 2021).

Another relevant factor is the particle size, which plays an important role in the separation of anode – cathode by flotation. Ultrafine oxide materials (particles with a size <10 µm) have a low probability of collision between particles and bubbles (Trahar and Warren, 1976). However, they still tend to be found in the concentrate, because they are entrained due to their small size (Shahbazi, Rezai and Koleini, 2010). This phenomenon is mainly controlled by the water recovery rate which is linearly correlated with the recovery of oxide materials (Jowett, 1966; Sajjad and Otsuki, 2022).

Several works have been reported using flotation as an efficient technique for separation of graphite from lithium metal oxides (LMO). Many report a high-grade of lithium metal oxides ranging between 50 per cent to 95 per cent in tailings and graphite grades between 80 per cent to 90 per cent in concentrates, depending on processing conditions and number of flotation stages (Yu *et al.*, 2018; Liu *et al.*, 2020). All these works involved testing industrial electrode materials which are not fully liberated (Vanderbruggen *et al.*, 2021), due to the binder employed in the agglomeration of graphite and lithium metal oxides particles.

In this paper, the separation behaviour of anode and cathode materials in a synthetic mixture of graphite and NMC-111 and using a commercial spent lithium ion battery based on NMC-111 technology is explored. This analysis includes the study of different processing conditions in a single batch flotation stage with the aim to maximise the graphite recovery in concentrates and maximise the recovery of lithium metal oxides in tailings.

## EXPERIMENTAL

In these experiments synthetic mixtures of electrode materials and real electrode materials taken from a spent commercial lithium-ion battery based on NMC-111 ( $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ ) technology were used in the flotation experiments. Given the heterogeneous nature of LIBs, a full characterisation analysis was carried out on feed materials. These analyses include particle size analysis, scanning electron microscopy, X-ray diffraction, X-ray fluorescence, chemical analysis, contact angle analysis, thermogravimetric analysis and mineral liberation analysis (MLA), both before and after high temperature roasting.

The spent electrode materials, were roasted under nitrogen atmosphere (2 L/min) at 600°C for 2 h in a laboratory furnace, in order to remove the organic binder in samples.

Batch flotation trials were conducted in a 0.5 L Denver cell using air as carrier gas at 180 L/h equivalent to 1.05 cm/s as superficial gas rate, and using a mixing speed of 900 rev/min, in order to minimise the hydrodynamic effect in the entrainment degree of these oxides in the graphite concentrates. The solid content in slurries was 13 per cent w/w for all experiments and the reagents used were 0.1 M NaOH, used as pH modifier, and kerosene, (reagent grade, Sigma-Aldrich, Australia), as collector for graphite in some of the experiments.

The electrode materials used in these experiments were pure graphite (>99.9 per cent purity, particle size 100 per cent <20 µm, Sigma-Aldrich, Australia) and lithium nickel manganese cobalt oxide ( $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ ), NMC-111, (>99.00 per cent purity,  $D_{50} = 7.5$  µm, MSE supplies, USA) and the anode and cathode material were taken from a spent lithium ion battery model JH3 from LG Chem and provided by Envirostream Australia Pty Ltd. The frothers evaluated in this study were 2-Octanol, 97 per cent purity, supplied by Sigma-Aldrich Australia, 4-Methyl-2-pentanol (MIBC) reagent grade, 98 per cent purity, supplied by Sigma-Aldrich, Australia and Aerofroth® 88, (2-Ethylhexanol, >99 per cent purity), supplied by Solvay Australia. Regarding the dosages of collector and frother used in these experiments these were 350 g/t and 30 mg/L respectively. The flotation products were characterised using X-ray diffraction analysis and elemental analysis (CHNS analysis) used to measure the composition of total carbon assumed as graphite. Then, based on these results, elemental recoveries were calculated and flotation kinetics and grade/recovery data determined.

## RESULTS

Characterisation results for the commercial battery electrode material before roasting, indicated a high agglomeration degree according SEM and MLA analyses with a content of carbon in cathode material between 5–6 per cent C, indicating the presence of the organic binder. After roasting, the organic content was reduced (down to 0.70 per cent C) in samples with a particle size 100 per cent <math>-38 \mu\text{m}</math>, indicating significant binder removal, even though SEM and MLA analyses indicated a persistent agglomeration. Additionally, contact angle analyses confirmed changes in contact angle values for cathode material when this material was roasted, indicating a beneficial effect of roasting in terms of imparting hydrophilicity.

Regarding flotation experiments, these were divided in two parts. The first part relates to experiments using synthetic mixtures of graphite and lithium nickel manganese cobalt oxide ( $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ , NMC-111) in a ratio 47 per cent for graphite and 53 per cent for NMC-111. Flotation results at pH 12 indicated a good separation efficiency (81.40 per cent) with a low entrainment degree of oxides in the graphite concentrates using the reagent Aerofroth® 88, where the cumulative recovery for graphite and NMC-111 at 8 minutes of flotation were 97.75 per cent and 18.35 per cent respectively.

Applying the same processing conditions used for the synthetic mixtures, the second set of experiments were conducted using real electrode materials which were roasted before processing. The feed grade for these materials was 38.16 per cent graphite and 61.84 per cent NMC-111 respectively. Flotation results at 8 min of flotation, indicated cumulative recoveries for graphite and NMC-111 of 94.44 per cent and 14.02 per cent respectively. High-grades of graphite (80.61 per cent) were obtained in concentrates with lower NMC-111 grades (19.39 per cent). In tailings the grades of graphite and NMC-111 were 11.20 per cent and 88.80 per cent respectively. These results indicate that the use of roasting is effective in terms of binder removal for cathode materials. The last statement is validated when the flotation kinetics (cumulative recovery versus time) of synthetic mixtures of graphite and NMC-111 is compared with the flotation kinetics of commercial materials. This is shown in Figure 2.

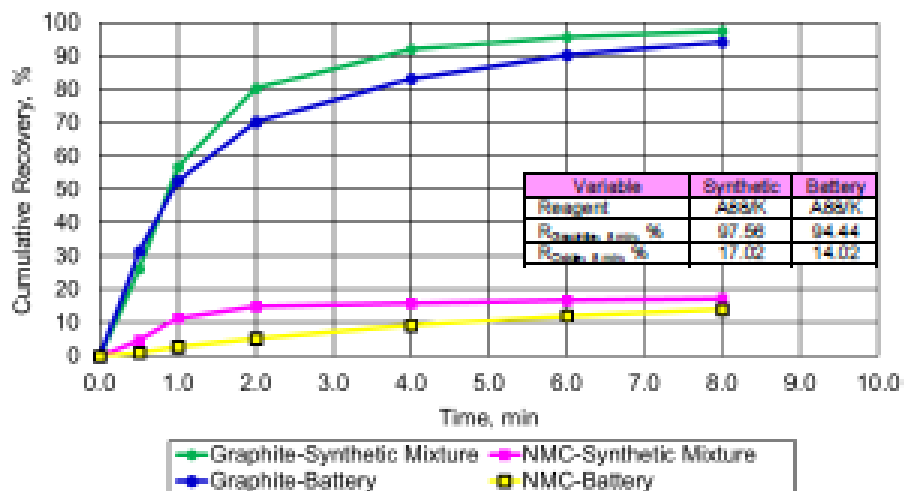


FIG 2 – Flotation Kinetics of Graphite and NMC-111 for each Experiment.

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