Boosting the Recycling Efficiency of Spent Lithium-Ion Battery Cathodes Using a Green Reductant

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One major bottleneck of today’s industrial hydrometallurgical lithium-ion battery recycling processes is the limited operation efficiency, particularly for leaching Co, Li, and Ni elements. Boosting the leaching rate and solid to liquid (S/L) ratio can increase the productivity and yield of recycled materials, which can save chemicals and energy cost. Herein, the use of ethylene glycol (EG), a green and sustainable reducing agent, for the separation of spent cathode materials resulting in high leaching efficiencies for very high loadings is demonstrated. The dramatically improved leaching efficiency is attributed to the EG reducing moieties that enable better cathode reduction and dissolution. The separation process avoids the use of toxic organic solvents, making the overall leaching process greener. The leaching efficiency is shown to remain high despite the use of high loadings as compared to the state-of-the-art works. The cathode separation process is then modified to allow for a facile separation of a cathode and anode mixture. This mixture is demonstrated to attain high leaching efficiencies at comparable loadings for cathode-only process. This redox leaching-based recovery process holds a potential for industry adoption due to the elimination of energy-intensive pretreatment step and the high efficiencies obtained.

1. Introduction

Lithium-ion batteries (LIBs) are currently the dominant means of energy storage with the ever-growing popularity of electric vehicles (EVs) and their continued use in consumer electronics. But, this exponential rate of production of LIBs is not even comparable to the rate of recycling, with a conservative estimate of it being less than 5%. LIBs contain a number of crucial elements such as Li, Co, Ni, Mn, Cu, and Al all of which if properly handled can be efficiently recovered.[2] As per an approximation done for a time period between 2015 and 2040 from EVs alone, 1.3 million metric tons of LIB waste are expected to be generated. A number of facilities have taken it up as a suitable recycling technology with companies such as Umicore pioneering the technology.[11] But, the pyrometallurgical process, despite being very simple and requiring no extra sorting and preprocessing, uses a huge amount of energy and generates a large amount of toxic gases, also Li and Al are lost in the process and cannot be recovered.[12]

Considering the disadvantages posed by the pyrometallurgical process, a number of corporates turned to the use of a solely hydrometallurgical process. The process involves leaching the elements from cathode materials and then recovering them either by solvent extraction or salt precipitation.[13] The main advantages of the process are that it recovers a high proportion of the battery elements and does not require a huge amount of energy.[14] A number of works have been focused on improving the leaching efficiency particularly for lithium nickel manganese cobalt oxide (NMC) cathodes. For example, Meshram et al. explored the use of a variety of reducing agents in combination with sulfuric acid with both hydrogen peroxide and sodium...
bissulfe reaching high leaching efficiencies but the optimal loading demonstrated was only 50 g L\(^{-1}\) for the former and 20 g L\(^{-1}\) for the latter.\(^{[15]}\) As a green alternative, Li et al. in multiple works have studied several organic acids for leaching resulting in excellent recovery but being limited by the optimal loading being attained of only around 40 g L\(^{-1}\).\(^{[16,17]}\) Thereby, a high amount of leaching solution is expended for the treatment of a small amount of cathode material which is inefficient. Works have also been limited by the type of cathode materials being treated with most treating either explicitly lithium cobalt oxide (LCO) or NMC-type materials and those treating a mixture of cathode materials showing a much lower leaching efficiency even at lower loadings.\(^{[18,19]}\)

In this work, we report the use of an adapted ethylene glycol (EG)-assisted cathode separation route, which boosted the overall leaching efficiency particularly at very high cathode powder loadings.\(^{[20–23]}\) The use of EG provides added reducing moieties to the cathode materials which aids the leaching process through the reduction of metal ions. We demonstrated high leaching efficiencies, i.e., above 95% for all elements under very high loadings of up to 100 g L\(^{-1}\) for a mixed LiNi\(_{0.5}\)Mn\(_{0.5}\)Co\(_{0.2}\) (NMC532) and LiMn\(_2\)O\(_4\) (LMO) cathode material, which could not be achieved via the conventional separation route. Furthermore, we expanded the applicability of the process through a facile modified extraction route which utilizes EG to extract a mixed cathode and anode powder. The mixture shows a comparable performance to that of leaching solely the cathode even at very high loadings. This significant improvement in the leaching efficiency can be attributed to the extraction process. The method discussed avoids the use of N-methyl-2-pyrrolidone (NMP) which is known to be difficult to handle due to its toxic nature whereas on the other hand, EG is environmentally benign and degrades quickly in nature. Therefore, its use simplifies the overall extraction process and makes it greener, enabling it to be more suitable for use at an industrial scale.\(^{[24–27]}\) This work potentially provides a recycling process that is eco-friendly in terms of both a more efficient utilization of the sustainable leaching solution as well as the use of a green agent for the cathode separation.

2. Result and Discussion

The work demonstrates an EG-based cathode active material separation process which facilitates very high leaching efficiencies even at very high loadings. The improvement in leaching efficiencies can primarily be attributed to the use of EG which provides additional reducing moieties to the cathode active powder as is shown by the comparison of leaching efficiencies for powders extracted by two different methods. Also, a novel modification of the process allows for leaching of cathode active materials without extensive cathode and anode separation and demonstrates leaching efficiencies comparable to that of leaching solely the cathode.

2.1. EG-Based Cathode Separation

In this work, both an EG-based and a conventional NMP-based cathode material separation process were followed to obtain cathode powder for the study of leaching kinetics. Figure 1 shows the differences in the processes utilized to extract the cathode powder. The conventional extraction method consists of immersing the cathode sheets in an NMP solution and heating it at 90°C for 8 h. The cathode active material was then scraped off from the current collector and centrifuged and washed. The obtained filtrate was then stirred in a solution of lithium and potassium hydroxide overnight to remove all traces of aluminum which may affect leaching efficiency (to avoid the effect of impurity in the leaching kinetics). Then to get rid of all the residual carbon black and PVDF, the powder was heated at 700°C for 5 h to finally obtain the cathode material powder. The EG-based process also consisted of a similar progression of steps with the only key difference being that the cathode sheets were treated in an EG solution by heating them at 90°C for 8 h. This allowed for the cathode active materials to be easily dislodged from the current collector when it was removed and filtered.

The powders were characterized to identify the differences in their structure caused by variation in the cathode separation method. X-ray diffraction (XRD) patterns of both the EG-based and NMP-based cathode powders are shown in Figure 2a. The cathode material consists of a mixture of NMC532 and LMO; peaks corresponding to both of the materials are observed in both the patterns. The peaks are relatively similar with only minor differences in peak intensity. For a few peaks, small shift to higher angles is observed for the powder extracted by the EG-based process as compared to the NMP-based powder. Even though there are very small differences present essentially, the extraction process does not majorly affect the bulk properties of the powder, and changes in crystallinity are not observed to have been caused. Although, leaching is considered to be a

Figure 1. Schematic illustration of conventional NMP versus EG-based cathode separation and extraction.
surface-controlled phenomenon—and any changes to the powder’s surface may be vital to the overall leaching efficiency observed. Figure 2b,c show scanning electron microscopy (SEM) images of the cathode powder obtained by the EG-based and NMP-based processes, respectively. A stark difference is observed between the images obtained in both the cases. The powder obtained by the EG-based process is seen to have an irregular shape of agglomeration which covers the entirety of the surface of the particles as compared to the NMP-based powder which is observed to have no additional agglomeration on the surface of the cathode particles. This morphology change is hypothesized to be caused by the use of EG in the separation process which imparts to the powder additional reducing moieties on its surface. Considering the surface-sensitive nature of the leaching process, the differences seen in the SEM images of the powder may be instrumental to the leaching efficiencies observed.

To further substantiate the hypothesis that reducing moieties are present in the case of the EG-based powder as compared to the NMP based one, X-ray photoelectron spectroscopy (XPS) analysis of the cathode powders was performed. Figure 3a shows the Co 2p3/2 spectrum for the EG- and NMP-based cathode powders. The deconvolution of the 2p3/2 is done to discern the relative presence of the different oxidation states present according to prior works,[28,29] with the Co3+ and Co2+ peaks identified at 779.9 and 777.2 eV, respectively. A peak from Co2+ is observed for the case of the EG-based powder whereas the NMP-based powder demonstrates only the Co3+ peak. Similarly, the ratio of the Mn4+ to Mn3+ peaks in Figure 3b

Figure 2. a) Comparison of XRD patterns of EG- and NMP-based extracted cathode powders. b) SEM image of EG-based cathode powder. c) SEM image of NMP-based cathode powder.

Figure 3. XPS data comparing the EG- and NMP-based cathode powders for a) Co 2p3/2, b) Mn 2p3/2, and c) Ni 2p3/2 spectra.
is seen to be 5:1 for the NMP-based powder whereas for the EG-based powder, there is a drastic increase in Mn$^{2+}$ species observed with a ratio of 1:1.44 (Mn$^{3+}$:Mn$^{2+}$).\cite{29,30,31} For the Ni 2p$^{1/2}$ spectra (Figure 3c), we can identify that the NMP-based powder shows a ratio of Ni$^{2+}$:Ni$^{3+}$ of 7.2:1, but for the EG-based powder, the presence of Ni$^{3+}$ is further diminished with a 16.8:1 ratio observed for Ni$^{2+}$:Ni$^{3+}$.\cite{32} All of these trends indicate the reduction of metal species in the cathode powder when using EG for cathode separation, supporting our hypothesis that the use of EG provides reducing moieties that result in partial reduction of the metals in the cathode powder which is responsible for more efficient leaching.

### 2.2. Leaching of EG-Based Cathode Powder

The hydrometallurgical recycling process used in the work consisted of a typical leaching setup where the spent cathode material was dissolved in a leaching solution and heated for a fixed amount of time with stirring. The typical leaching solution adopted here was a mixture of sulfuric acid (H$_2$SO$_4$) with hydrogen peroxide (H$_2$O$_2$) which is commonly used and has demonstrated reasonably high leaching efficiencies in several previous works.\cite{16,18,19} Figure 4a shows the leaching process where elements are extracted from the cathode powder in the form of metal sulfates and are present in the solution.

For the leaching process, four parameters including H$_2$SO$_4$ concentration, H$_2$O$_2$ concentration, cathode mass loading, and time were varied and the leaching efficiency was noted with the variation of the parameters. The initial parameters utilized were a mass loading of 50 g L$^{-1}$, a H$_2$O$_2$ concentration of 2% v/v (volume by volume), a temperature of 80 °C, a leaching time of 90 min, and the acid concentration was varied from 0 to 3 M.

Figure 4b shows that the optimal acid concentration was determined to be 2 M with leaching efficiencies close to a 100% obtained as the higher acid concentration shows relatively similar efficiencies. Generally, an increased concentration would result in better leaching, but beyond an optimal acid concentration, the increase in leaching efficiency is minimal.

To investigate the effect of H$_2$O$_2$ concentration, it was varied from 0 to 5% v/v while keeping all other parameters constant. A leaching efficiency of almost a 100% is noted for all the elements (Figure 4c) at a peroxide concentration of 2% (v/v) where with a higher concentration no significant increase was observed. As a result, a 2% (v/v) H$_2$O$_2$ concentration was deemed optimal. The role of H$_2$O$_2$ is to reduce cobalt from Co$^{3+}$ to Co$^{2+}$ and manganese from Mn$^{4+}$ to Mn$^{2+}$ making its concentration vital.

Figure 4d shows the variation of leaching efficiency with mass loading, i.e., mass of cathode per leaching solution, a leaching efficiency of 98% for Mn and Co and 99% for Ni, and Li is observed for a mass loading of 100 g L$^{-1}$. Even at high mass loadings of 75 and 100 g L$^{-1}$, the leaching efficiency remains just as high as that for lower loadings, so the optimal loading was chosen to be 100 g L$^{-1}$. Figure S1, Supporting Information, demonstrates a comparison of the leaching efficiency with a few previous works which utilize an acid and peroxide-based leaching solution for NMC cathode materials, most of the works could not achieve loadings greater than 40 g L$^{-1}$ and the works that did show significant drops in leaching efficiency at higher loadings.

Furthermore, we studied the effect of time on leaching efficiency for a loading of 100 g L$^{-1}$ by varying the leaching time from 15 to 90 min. In Figure 4e, we observe that initially at 15 min we have a leaching efficiency of 96% for Mn, 88% for Ni, 93% for Co, and 95% for Li, and with an increase in the leaching time to 45 min, the efficiency is seen to increase to nearly a
100% for Mn, Co, and Li and reached around 94% for Ni. With a further increase in leaching time, the efficiency remains relatively stagnant and so 45 min was deemed optimal for the leaching process.

The exceptionally high leaching efficiency observed for significantly high loadings with short leaching times is thought to be caused by the difference in the cathode separation method that we hypothesize forms additional reducing moieties due to the use of EG. Such a green solvent aids in the reduction of the states of the metallic ions making the leaching process simpler. Figure 4f shows a comparison of the efficiencies for various loadings for EG- and NMP-based cathode powders, we can see a higher leaching efficiency for the EG-based cathode separation route, thus confirming our hypothesis that the presence of reducing moieties due to the use of EG benefits the leaching process.

To demonstrate the high loading capabilities for leaching via the adapted EG-based method, the results obtained were contrasted with the state-of-the-art works that studied leaching of LIB materials. Figure 5 shows the leaching efficiencies for Co and Li (the most difficult to leach elements) at optimal loadings compared with several works that leached either LCO, NMC, or a mixture of various cathode chemistries. Our work demonstrated a high leaching efficiency at significantly higher loadings whereas some other works despite achieving high leaching efficiencies were limited by the loading that can be utilized. A higher loading implies a more optimal and efficient use of the leaching solution thereby making the overall recycling loop more sustainable.

To further establish the sustainability of the process, the capacity to reuse EG was demonstrated by recovering EG after using it for cathode separation and using it again for separation by multiple times. The cathode powder from each subsequent use of the EG solution for cathode separation was recovered and processed and then leached in the same system under the optimal leaching conditions determined previously, maintaining high loading of 100 g L⁻¹. Figure S4. Supporting Information, shows the leached solution for cathode material separated using fresh EG, EG used once, and EG used twice; all of them appear to be fully leached with no residue observed to settle at the bottom. This shows that the EG solution can be reused multiple times and continues to remain effective, making the overall process even more green and sustainable.

2.3. Leaching of Mixed Cathode and Anode Powder

To reduce the refinement required for the leaching process, the separation process was modified to directly obtain a mixture of cathode and anode powder. Figure 6a shows a schematic of the novel modified treatment process where cathode and anode were cut into small pieces and heated overnight in EG at 90 °C. Cathode and anode powders were dispersed in the EG solution. It was then filtered and the current collectors were separated. The obtained powder was then directly subjected to leaching in the same way as the previous powder without any additional treatment. After the leaching process, the solution is filtered to remove the graphite powder. We studied the leaching efficiencies obtained using the modified process and contrast it to that of the initial EG-based process for only the cathode. Figure 6b-e show that the leaching efficiencies for Co, Li, and Mn for high cathode loadings are comparable to that of the EG-based cathode powder and that of Ni is only slightly affected by the modified process. This modified process removes the initial pretreatment and separation required for cathode and anode as well as the sintering step, making the overall leaching process simpler and still attaining equally high leaching efficiencies for high loadings. The method can also potentially be used in the industry directly due to the elimination of the preprocessing requirement and the facilitated direct battery leaching. To be able to claim that the EG-based process for mixed cathode and anode is the sole reason for an improved leaching efficiency, we also examined and compared the leaching efficiencies for the EG-based mixed cathode and anode with the NMP-based mixed powder which was not heated for 5 h at 700 °C to ensure an even comparison. We see a large difference between the leaching efficiency of the mixed cathode and anode powder with it being nearly 40% higher for Mn, Ni, Co, and Li for the high loading used in the EG system (Figure S2, Supporting Information). This improved efficiency can clearly be attributed to the use of EG which gives reducing moieties to the powder thereby aiding metal reduction and boosting leaching.

2.4. Metal Salt Recovery

To recover the metal ions in a form that can be reused for further synthesis of electrode materials, Co, Li, Mn, and Ni were recovered as metal salts through salt precipitation. Figure S3, Supporting Information, shows a schematic of the salt precipitation and extraction process which is based on a method used in a previous work. To the leached solution, first oxalic acid was added to recover cobalt as cobalt oxalate and it was then centrifuged and separated to reobtain the leached solution. The pH of the solution was then increased to obtain a pH of 7.5 using a 2 M NaOH solution. After attaining the required pH, a saturated
solution of sodium bicarbonate was added to recover manganese as manganese carbonate. After separating the salt, to the sodium hydroxide solution was again added to attain a pH of 9 and to this sodium bicarbonate was added to precipitate nickel as nickel carbonate. Finally, lithium carbonate was recovered by further increasing the pH to 11.5 by adding sodium bicarbonate. The recovery efficiency for the various elements was seen to be 92% for Co, 90% for Li, 90% for Mn, and 93% for Ni. Although there remains a small fraction of residual metal ions to be claimed from the leaching solution, we showed significant advancement in the leaching process using a green, efficient and low-cost reductant. Further optimization on the salt precipitation steps with a larger size of operation batch will lead to fine control of elemental recovery, which is a focus of a different topic in our research.

3. Conclusion

In summary, in this work, we have demonstrated an EG-based separation and leaching method which resulted in significantly higher leaching efficiencies for LIBs cathode materials. Particularly, compared to prior works much higher cathode loadings could be achieved for the leaching process resulting in more efficient utilization of the leaching solution. The leaching efficiency of the powder was shown to be higher than that of the powder extracted by the NMP-based route and this enhancement in efficiency was shown to be solely caused by the use of EG which imparts reducing moieties to the cathode powder aiding reduction of elements and improving the leaching process. Furthermore, a modification in the separation process was demonstrated where less refinement was required and a mixed cathode and anode powder was obtained thereby simplifying the pretreatment needed. The modified industrially applicable process showed an equally high leaching efficiency as leaching solely the cathode powder and the novel method did not show any depletion in efficiency even at high loadings. The metal salts were also shown to be recovered by a facile salt precipitation-based process that did not require any additional expensive chemical agents and yet showed reasonably high extraction efficiencies. To further enhance the metal recovery efficiency, in future works, the solution post metal extraction can be combined with a freshly leached solution and the process can be repeated, which can create a cascaded process to ensure almost full salt extraction from the leached solution. This will not only enhance recovery efficiency but also minimize waste regeneration. The salt extraction using the same process can also be refined in the future to avoid salt separation and rather use the leached solution for the direct synthesis of high-capacity cathode materials. The overall leaching process is seen to be simple, efficient, and practical with the use of EG significantly improving the leaching efficiency. We expect that continuous improvement of the extent of scaling can simplify and practically integrate our approach into the industrial leaching process.

4. Experimental Section

Materials and Reagents: Spent LIBs were General Motor’s Chevrolet Volt EV cell (20 Ah) in which the cathode material composition was specified as a mixture of 66 wt.% of LiNi$_{0.2}$Mn$_{0.3}$Co$_{0.4}$ and 33 wt.% LiMn$_2$O$_4$. All the reagents were of an analytical grade and were appropriately diluted using distilled water to lower concentrations.

EG-Based Cathode Material Extraction: In an inert environment, the battery was opened and separators removed to separately collect each cathode sheet. These sheets were immediately immersed in a DEC solution for 2 h to remove all residual traces of electrolyte. The cathode sheets were then washed and dried at 80 °C overnight. The sheets were cut up to have dimensions of $\approx 10 \text{cm} \times 8 \text{cm}$ and were placed in $\approx 400 \text{mL}$ of EG solution and heated overnight at 90 °C. The cathode powder was then easily removed from the current collector by scraping it off. It was then stirred in a solution of 3 M KOH and 0.5 M LiOH overnight. It was washed twice with a 0.2 M LiOH solution to remove excess KOH to maintain the
original state of the cathode powder. The powder was filtered from the solution and dried at 80 °C overnight to obtain the cathode active material. This powder was again heated at 700 °C for 5 h in a muffle oven and stored for future use.

Mixed Anode and Cathode Materials Extraction: A similar process was followed to obtain the mixed cathode and anode materials. In an inert environment, the battery was opened and cathode and anode sheets were recovered. All traces of electrolyte were removed by immersing them in a DEC solution and then washing them with water and drying them at 80 °C overnight. The cathode and anode sheets were then cut up into small pieces of ≈2 cm × 2 cm and stirred overnight in an EG solution heated to 90 °C. The mixed cathode and anode powder was dispersed in the EG solution and filtered. The filtrate was then dispersed in a solution of 3 M KOH and 0.5 M LiOH and stirred overnight to remove remnant traces of aluminum. It was washed twice with a 0.2 M LiOH solution to remove excess KOH without changing the status of the cathode powder. The powder was filtered from the solution and dried at 80 °C overnight to obtain the mixture of anode and cathode active material.

Leaching of Powder: For the study of the leaching kinetics, a total volume of 10 mL of leaching solution was used, appropriate amounts of H₂O₂ and H₂SO₄ were used and diluted to the required concentration. Fixed amount of powder was added to this solution based on the mass loading. The solution with the powder was placed in a hot oil bath and continuously stirred for a fixed time period at 80 °C. After leaching, the solution was removed from the oil bath and then subjected to inductively coupled plasma mass spectrometry (ICP–MS) to determine the leaching efficiency. For the case of the NMP un-sintered powder and the mixed cathode and anode powder, additional filtration step was required to remove the graphite/carbon particles that remained to obtain the leached solution.

Metal Salt Separation and Extraction: 50 mL of the leached solution was taken in a beaker and according to the approximate cobalt concentration, a stoichiometrically equivalent amount of oxalic acid was added to form cobalt oxalate.[37] Cobalt oxalate was separated from the leached solution by centrifugation and washed twice with water and once with ethanol before drying it at 80 °C for 3 h. The filtered solution’s pH was then increased to 7.5 by using an appropriate amount of 2 M NaOH and to this Na₂CO₃ was added to precipitate the salt.[42] The obtained manganese carbonate was centrifuged and washed similarly and then dried at 80 °C for 5 h to obtain the metal salt. The separated solution’s pH was further increased to 9 and Na₂CO₃ was added at the required pH to precipitate the nickel salt. It was again centrifuged and washed and then dried overnight at 80 °C to obtain metal salt. Finally, the filtrate solution’s pH was increased to 11.5 and Na₂CO₃ added again. This was then centrifuged and washed in the same way and dried at 80 °C overnight to obtain lithium carbonate.

Characterization: The metal (Li, Ni, Mn, and Co) concentrations were determined by using quadrupole mass spectrometer (ICP–MS, Thermo Scientific, iCAP RQ model). The leaching efficiency was quantified as the ratio between concentration of the element in the leached solution to the leaching efficiency obtained for a loading of 30 g L⁻¹ which is considered to be fully leached.

The structure of the cathode material was studied using XRD by employing a Bruker D2 Phaser (Cu Kα radiation, λ = 1.5406 Å) with a scanning rate of 0.5° min⁻¹. The surface structure and morphology of the cathodes obtained by EG- and NMP-based separation methods was examined by SEM (FEI XL30).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Z.C. conceived the idea, designed the experiment, and directed the project. S.R. conducted material processing, kinetics studies, and analyzed the data. P.X. conducted ICP measurements. M.L. and Y.X. performed XRD measurements and obtained SEM images and aided in their analysis. P.X. and H.G. revised the article. All authors discussed the results and commented on the article.

Data Availability Statement

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

Keywords

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