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Improving Extraction Efficiency by Chemical and Process Design Optimization for Elemental Recovery from Waste Lithium-Ion Battery Cathodes

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Rose, Satchit

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Improving Extraction Efficiency by Chemical and Process Design Optimization for Elemental Recovery from Waste Lithium-Ion Battery Cathodes

A thesis submitted in partial satisfaction of the requirements

for the degree of Master of Science

in

Nanoengineering

By

Satchit Rose

Committee in charge:

Professor Zheng Chen, Chair
Professor Ping Liu
Professor Shirley Meng

2021

The thesis of Satchit Rose is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

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Chapter 2, in full, is a reprint of the material as it appears in Advanced Energy and Sustainability Research 2021. Rose, Satchit; Xu, Panpan, Gao, Hongpeng; Li, Mingqian, Yu, Xiaolu; Zheng Chen, Wiley-VCH 2021. The thesis author was the primary investigator and author of this paper.

Chapter 3 is coauthored with Yu, Xiaolu; Gao, Hongpeng and Chen, Zheng. The thesis author was the primary author of this chapter.

ABSTRACT OF THE THESIS

Improving Extraction Efficiency by Chemical and Process Design Optimization for Elemental Recovery from Waste Lithium-Ion Battery Cathodes

by

Satchit Rose

Master of Science in Nanoengineering

University of California San Diego, 2021

Professor Zheng Chen, Chair

The modern industrial hydrometallurgical recycling process is majorly constricted by process efficiency and generalizability reflected in the limited recovery of elements like Mn and Ni in particular. Enhancement of the recovery efficiency and the solid to liquid ratio (S/L ratio) as well as optimizing the process is vital to reducing energy and chemical costs to make the recycling loop more sustainable and environmentally friendly. In this work we demonstrate two novel hydrometallurgical recycling approaches harnessing chemical and process design optimization to boost leaching efficiencies. The first utilizes ethylene glycol known as an effective alternative green cathode separation agent and demonstrates significant improvements in leaching efficiency even at very high cathode loadings. The process mitigates the use of toxic solvents and compared to state-of-the-art works is suitable for high loadings. It was then further expanded for the recovery of a mixed cathode and anode powder with equally high cathode loadings and showed no dip in leaching efficiency. In the second approach we developed a novel recycling process that takes advantage of the multi-faceted effect of an alternative heating mechanism to yield high leaching efficiencies in significantly shorter time periods. Compared to conventional heating the new process achieved high leaching efficiencies at high loadings in only a fraction of the time. The elemental extraction was also demonstrated to be unanimously efficient with a wide variety of cathode chemistries. We believe that these methods are promising for industrial scale recycling avoiding excess chemical and energy utilization.

Chapter 1: Introduction

Lithium-ion batteries are quickly becoming the dominant technology for global energy storage with their widespread usage in a number of fields including electronics, electric vehicles and even grid storage. In 2017 alone nearly 670 tons of lithium-ion batteries were sold around the world. [1] The rapidly rising population is further increasing this energy storage demand with the lithium-ion battery demand as of 2020 estimated to be around 220 GWh/ year and projected to increase nearly tenfold in the coming decade. [2] This LIB market growth is primarily attributed to the expansion of electric vehicles with almost 75% of the demand in 2025 projected to arise from the use of electric vehicles. [3] The popularity of lithium-ion batteries can primarily be attributed to their high specific capacity, energy density, longevity and ease of assembly. But such a widespread demand and usage of LIBs also implies a large amount of waste batteries once they attain the end of their lives. Waste batteries bring with them a number of issues which include not only the safety risk and environmental consequences posed by their improper disposal but also the immense economic value they possess. An estimated 600000 waste batteries are expected to be produced by 2030. [4] While other estimates place the total amount of waste EV batteries between 2015 and 2040 up to 4 million metric tons but even a conservative estimate of 1.3 million metric tons holds an economic value of 3 billion USD considering 100% recovery of all elements. [3] Apart from the cost factor involved the sustainability of battery production is threatened by the limited and highly geographically centered nature of the metal reserves particularly cobalt, whose price and availability are highly uncertain. [5] This is particularly prominent considering that a majority of LIBs reaching the end of their lifetimes currently have mainly Lithium Cobalt Oxide (LCO) and $LiNi_{0.3}Mn_{0.3}Co_{0.3}$ (NCM 111) type chemistries with a higher cobalt content which also explains their higher supply risk and market value. [6] Even lithium extraction consumes tremendous amounts of water where a ton of lithium needs nearly 1900 tons of water with its reserves also concentrated mainly in Chile and Australia. [7] Though LIB manufacturers are currently shifting to higher nickel contents, waste batteries with increased cobalt contents continue to pile up emphasizing the need for reuse or recycling. [8]

Batteries often retain up to 75% of their capacity at the end of their lives from their primary application so they can be redirected to other applications such as grid storage where capacity requirements and cycling conditions are less demanding. [9] But eventually the spent batteries would have to be recycled to mitigate the impacts of improper disposal and to recover the transition metals present. Currently industrially implemented recycling techniques primarily comprise of pyrometallurgical and hydrometallurgical recycling. [10-12] Pyrometallurgy utilizes extremely temperatures as high as 1400°C to smelt the metals and burn away the separator and other components. [13] The metal mixture is then further processed using hydrometallurgy and solvent extraction agents to recover the various metals. Several recycling plants have taken it up as a suitable recycling technology with Umicore being one of the first to adopt it. Umicore utilizes an ultra-high temperature method which handles large volumes and forms a Ni-Co-Cu alloy slag which is then treated to recover each element. [14] Though, even considering the facile nature of the process and the lack of pre-processing required it has a number of challenges which include the use of a copious amount of energy, the inability to recover lithium and aluminum and release of a lot of toxic gases. [15]

Taking into account the disadvantages posed by pyrometallurgy the industry shifted to the use of a purely hydrometallurgical recycling process. The process comprises of leaching elements from cathode materials using a leching solution followed by treatment by solvent extraction agents or salt precipitation to recover the various metal salts. [16] Its primary advantages are that it recovers all the various elements, has very high recovery efficiencies and requires significantly less energy.

A lithium-ion battery essentially comprises of a cathode, anode, electrolyte, separator and a casing within which all of these are enclosed. The cathode itself consists of an aluminum current collector onto which a mixture of the cathode active material, carbon (enhance conductivity) and polyvinylidene fluoride (PVDF) (provides adhesion) is cast. [17,18] So prior to the leaching process the cathode active material would have to be extracted from the spent LIBs by discharging and dismantling them first. The discharge process can either be a physical or a chemical one. [19,20] For physical discharge the spent batteries are caused to short circuit by perforating them and releasing residual charge. On the other hand, chemical discharge uses solutions such as Na_2SO_4 and NaCl which are conductive to facilitate energy release. The cathode materials are then separated from metals, plastics and anode materials by first crushing the spent batteries and then using froth flotation and density separation. [21,22] A number of pretreatment strategies are currently used but their primary purpose is to minimize the presence of impurities and ensure a clean separation of cathode active materials.

The leaching solution consists of a combination of a strong inorganic or mineral acid like hydrochloric or sulfuric acid with a potent reducing agent like hydrogen peroxide. Works in the field initially focused on the recycling of Lithium Cobalt Oxide (LCO) batteries due to their prevalence in consumer electronics. Sun *et al.* and Swain *et al.* demonstrated the use of a typical sulfuric acid- hydrogen peroxide leaching system with leaching efficiencies greater than 90% for lithium and cobalt. Primarily to maximize the leaching efficiency these works optimized the reducing agent concentration, acid concentration, leaching time, solid to liquid ratio and temperature. [23,24] Recent works seek to optimize the leaching efficiencies of NMC cathodes in particular due to their dominant use in electric vehicles (EV). Meshram *et al.* studied the impact of numerous reducing agents combined with sulfuric acid on the leaching efficiency and attained fairly high leaching efficiencies but specifically for hydrogen peroxide utilized a low optimal loading of 50 g/L and for sodium bisulfite only 20 g/L. [25] Exploring a greener option, Li *et al.* utilized a variety of organic acids for leaching and demonstrated very high leaching efficiencies but were limited by a material loading of only 40 g/L. [26,27] While other works like that of Zhao *et al.* investigated a sulfuric acid-based system with ethanol as the reducing agent and even at comparatively low loadings of 40 g/L showed a decline in leaching efficiencies. [28] Seeking an alternative, researchers explored the use of alkaline agents, Qi *et al.* studied the use of a combined $NH_3.H_2O$-NH_4HCO_3 and Na_2SO_3 system showing high leaching efficiencies for cobalt and lithium but limited by the mass loading that was used, while Vieceli *et al.* demonstrated the use of sodium metabisulphite as a leaching solution with fairly high loadings but attaining low efficiencies of only upto 60%. [29,30] Low loadings result in the use of a large amount of leaching solution for recycling a relatively small amount of active material constraining the sustainability of the process. Most prior works also discuss the leaching of only a particular cathode material while works exploring the recovery of a mixture of cathode materials demonstrated a significant dip in leaching efficiency. [31,32]

Apart from low loadings utilized in prior works another issue reducing the feasibility of the process is the amount of time taken for the leaching process. In state of the art works the leaching itself takes anywhere between 1 to 3 hours for complete leaching. For example, Zhu *et al.* utilizing the typical sulfuric acid- hydrogen peroxide system took about 2 hours in order to attain high leaching efficiencies. [33] Similarly, in the work by Chen et al. we observe that to achieve high leaching efficiencies it takes up to 90 minutes using a citric acid based leaching solution. [34]

While green alternatives such as bioleaching shown by Mishra D *et al.* take several days and still demonstrate only moderate leaching efficiencies. [35]

Finally, after leaching, the metal products are recovered as metal salts by using either solvent extraction and salt precipitation or only the latter. In solvent extraction the metals are separated from one another by adding various chemical agents to the leaching solution. Na-D2EHPA is often used to separate cobalt and manganese while Na-Cyanex 272 is utilized for the separation of cobalt and nickel and DMG is seen to be effective in the segregation of nickel and lithium and these chemicals demonstrate high separation efficiencies and purities greater than 90%. [36,37] After segregation the metals can then be recovered as metal carbonates or hydroxides, the salt precipitation can also be used independently by using NaOH to control pH of the leaching solution and adding sodium bicarbonate at specific pH values to recover metal carbonates. [38]

Chapter 2: Boosting the Recycling Efficiency of Spent Lithium-Ion Battery Cathodes using a Green Reductant

In this chapter, 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. [39-41] 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 for a mixed $LiNi_{0.5}Mn_{0.3}Co_{0.2}$ (NMC532) and $LiMn_2O_4$ (LMO) cathode material, which could not be achieved via the conventional separation route. Further 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 while on the other hand EG is environmentally benign and degrades quickly in nature. Thereby, its use simplifies the overall extraction process and makes it greener, enabling it to be more suitable for use at an industrial scale. [42-45] 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.

2.1 Experimental methods

Materials & Reagents:

Spent LIBs were General Motor's Chevrolet Volt EV cell (20Ah), in which the cathode material composition was specified as a mixture of 66 wt.% of $LiNi_{0.5}Mn_{0.3}Co_{0.2}$ and 33wt.% $LiMn_2O_4$. 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 hours to remove all residual traces of electrolyte. The cathode sheets were then washed and dried at 80 ^{o}C overnight. The sheets were cut up to have dimensions of approximately 10 cm * 8 cm and were placed in approximately 400 ml of EG solution and heated overnight at 90^{o}C. The cathode powder was then easily removed from the current collector by scraping it off. It was then stirred in a solution of 3M KOH and 0.5M 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^{o}C overnight to obtain the cathode active material. This powder was again heated at 700 ^{o}C for 5 hours 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^{o}C overnight. The cathode and anode sheets were then cut up into small pieces of approximately 2cm * 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 3M 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 H_2O_2 and H_2SO_4 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.[46] 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 hours. The filtered solution's pH was then increased to 7.5 by using an appropriate amount of 2M NaOH and to this Na_2CO_3 was added to precipitate the salt.[38] The obtained manganese carbonate was centrifuged and

washed similarly and then dried at 80 °C for 5 hours to obtain the metal salt. The separated solution's pH was further increased to 9 and Na_2CO_3 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 Na_2CO_3 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 which is considered to be fully leached.

The structure of the cathode material was studied using X-ray diffraction (XRD) by employing a Bruker D2 Phaser (Cu Kα radiation, $\lambda = 1.5406$ Å) with a scanning rate of 0.58 deg/min. The surface structure and morphology of the cathodes obtained by EG- and NMP-based separation methods was examined by scanning electron microscopy (SEM, FEI XL30).

2.2 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 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.

2.2.1. EG based cathode separation

In this work, both an EG-based and a conventional NMP-based cathode material separation process was followed in order 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 hours. The cathode active material was then scrapped 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 in order to get rid of all the residual carbon black and polyvinylidene difluoride (PVDF), the powder was heated at 700 °C for 5 hours 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 hours. This allowed for the cathode active materials to be easily dislodged from the current collector when it was removed and filtered.

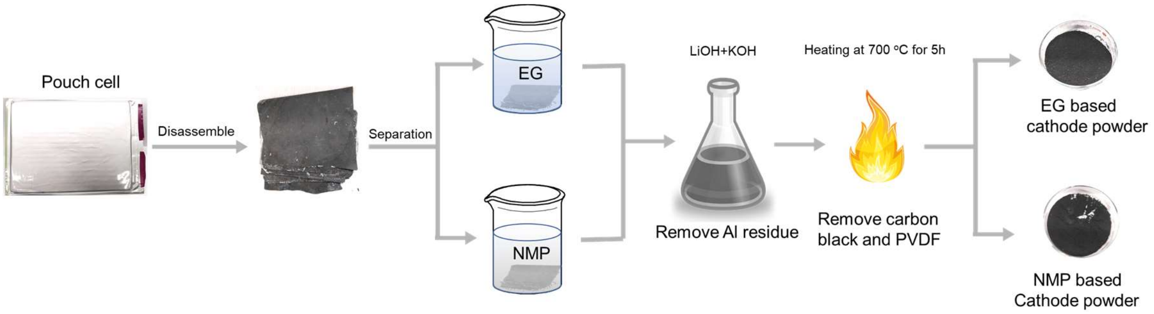

Figure 1. Schematic illustration of NMP vs. EG based cathode separation and extraction.

2.2.2. Leaching of EG-based cathode powder

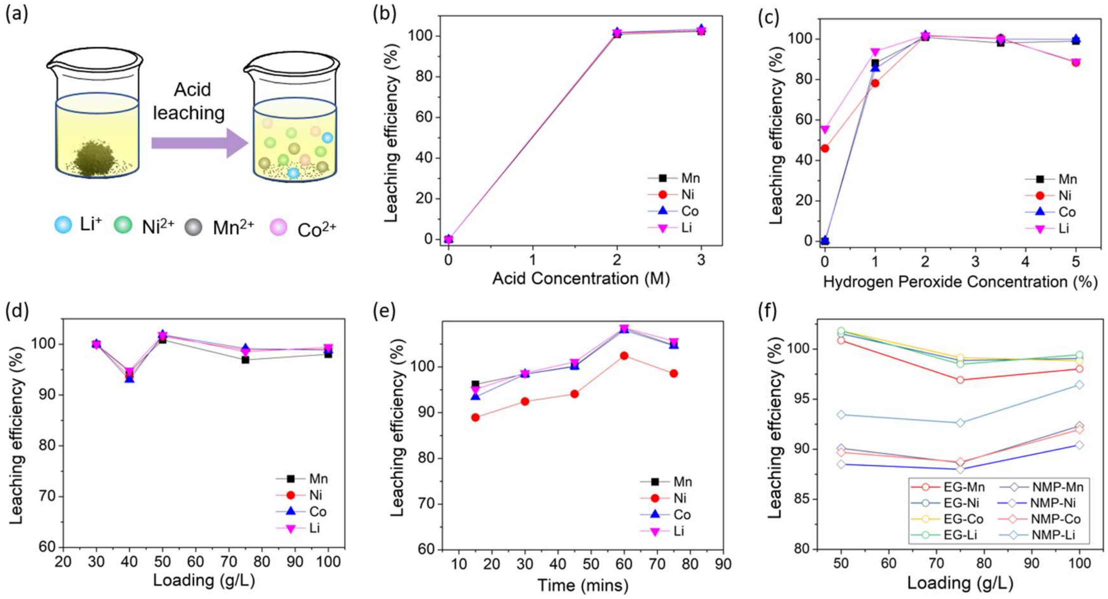

Figure 2. a) Scheme illustration of the leaching process. Variation of leaching efficiency with b) acid concentration, c) H_2O_2 concentration, d) mass loading and e) time; f) Comparison of leaching efficiency of EG- and NMP-based extraction methods.

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_2SO_4) with hydrogen peroxide (H_2O_2) which is commonly used and has demonstrated reasonably high leaching efficiencies in several previous works. [26,31,32] Figure 2(a) 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_2SO_4 concentration, H_2O_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, a H_2O_2 concentration of 2% v/v (volume by volume), a temperature of 80ºC, a leaching time of 90 minutes and the acid concentration was varied from 0 to 3M. Figure 2b shows that the optimal acid concentration was determined to be 2M 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_2O_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 2c) 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_2O_2 concentration was deemed optimal. The role of H_2O_2 is to reduce cobalt from Co^{3+} to Co^{2+} and manganese from Mn^{4+} to Mn^{2+} making its concentration vital.

Figure 2d 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. Even at high mass loadings of 75 and 100 g/L the leaching efficiency remains just as high as that for lower loadings, so the optimal loading was chosen to be 100 g/L.

Further we studied the effect of time on leaching efficiency for a loading of 100 g/L by varying the leaching time from 15 to 90 minutes. In Figure 2e we observe that initially at 15 minutes we have a leaching efficiency of 96% for Mn, 88% for Ni, 93% for Co and 95% for Li, and with an increase of the leaching time to 45 minutes 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 minutes 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 2f 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, further strengthening 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. [23,25,28,35,46-51] Figure 3 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 in spite of achieving high leaching efficiencies were limited by the loading that could be utilized. A higher loading implies a more optimal and efficient use of the leaching solution thereby making the overall recycling loop more sustainable.

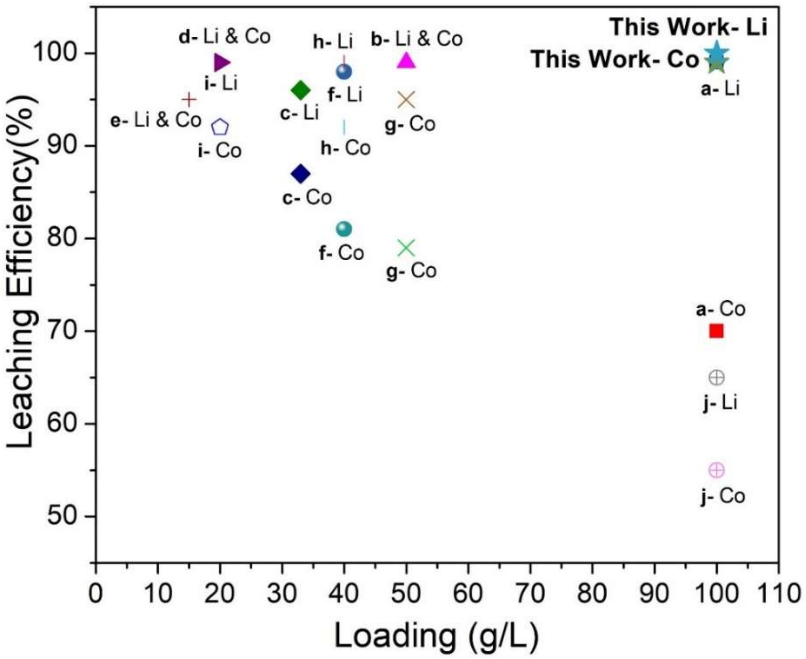

Figure 3. Comparison of leaching efficiencies of Co and Li between prior works and this work. a- Jha M.K. et al., [47] b- Sun L et al., [23] c- Zhu S. et al., [35] d- Wang R.C. et al., [48] e- Fu Y. et al., [46] f- Zhao J. et al., [38] g- Meshram P. et al., [25] h- Gao W.F. et al., [49] i- Chen X.P. et al., [50] j- Vieceli N. et al. [51]

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 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. Figure 4 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.

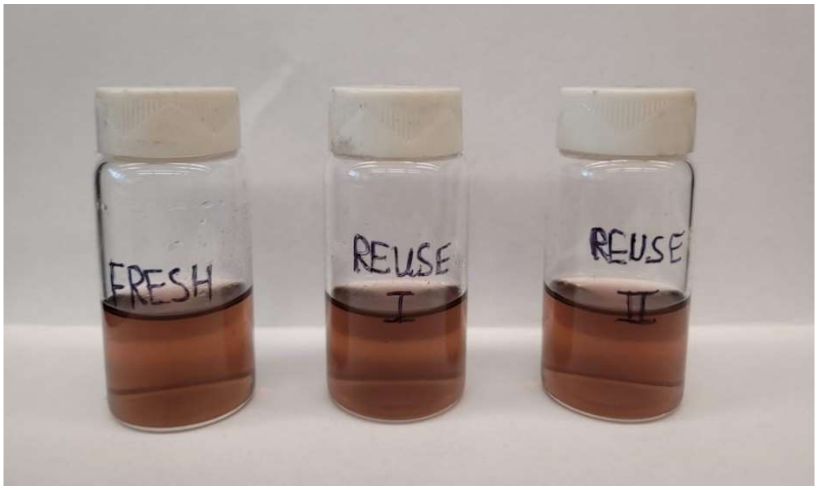

Figure 4. Leached solutions from cathode powder obtained using fresh EG solution, once reused solution and twice reused solution for cathode separation (left to right)

2.2.3. Characterization of cathode powder

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 5a. 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 surface-controlled phenomenon and any changes to the powder's surface may be vital to the overall leaching efficiency observed. Figure 5b and c show 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.

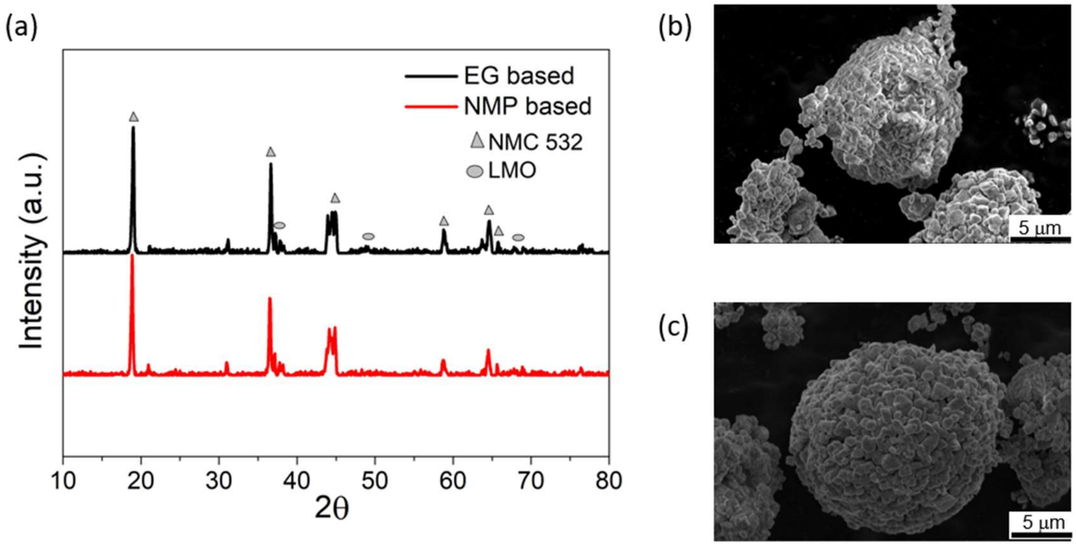

Figure 5. a) Comparison of XRD patterns of EG- and NMP-based extracted cathode powders. b) SEM image of EG-based cathode powder. c) SEM image of NMP-based cathode powder.

In order to further substantiate the hypothesis that reducing moieties were 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 6(a) shows the Co $2p_{3/2}$ spectrum for the EG and NMP based cathode powders. The deconvolution of the $2p_{3/2}$ is done to discern the relative presence of the different oxidation states present according to prior works [52,53], with the Co^{3+} and Co^{2+} peaks identified at 779.9 and 777.2 eV respectively. A peak from

Co^{2+} is observed for the case of the EG based powder while the NMP based powder demonstrates only the Co^{3+} peak. Similarly, the ratio of the Mn^{4+} to Mn^{3+} peaks in Figure 6(b) is seen to be 5:1 for the NMP based powder while for the EG based powder there is a drastic increase in Mn^{3+} species observed with a ratio of 1:1.44 (Mn^{4+}: Mn^{3+}). [54,55] For the Ni $2p^{3/2}$ Figure 6(c) spectra as well 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+}. [56] 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 and boost the leaching efficiency.

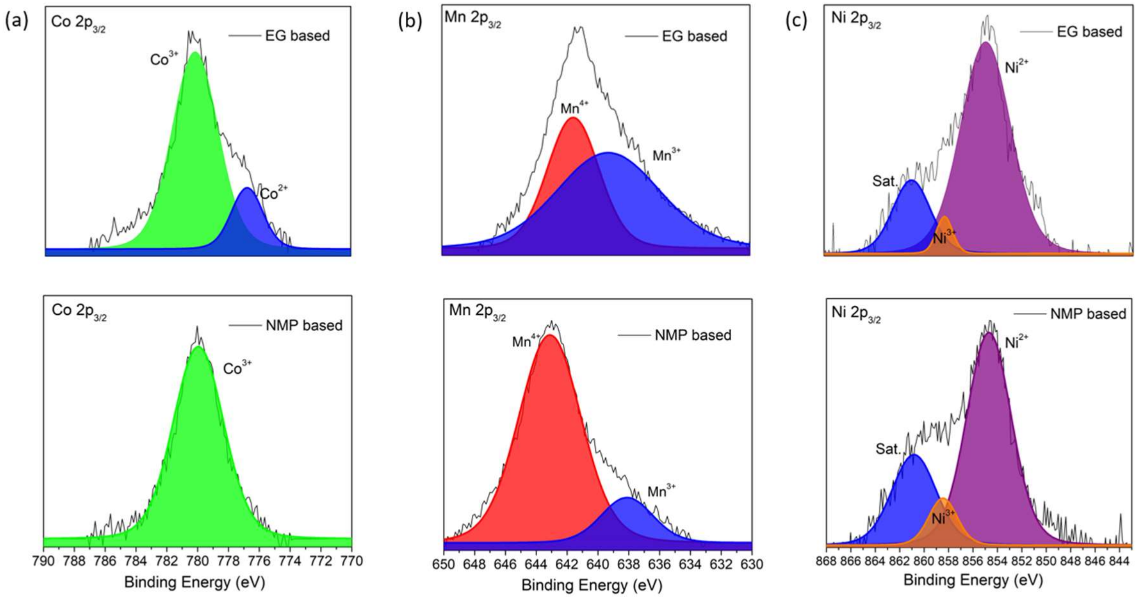

Figure 6. XPS data comparing the NMP and EG based cathode powders for a) Co $2p_{3/2}$ b) Mn $2p_{3/2}$ c) Ni $2p_{3/2}$ spectra

2.2.4. Leaching of mixed cathode and anode powder

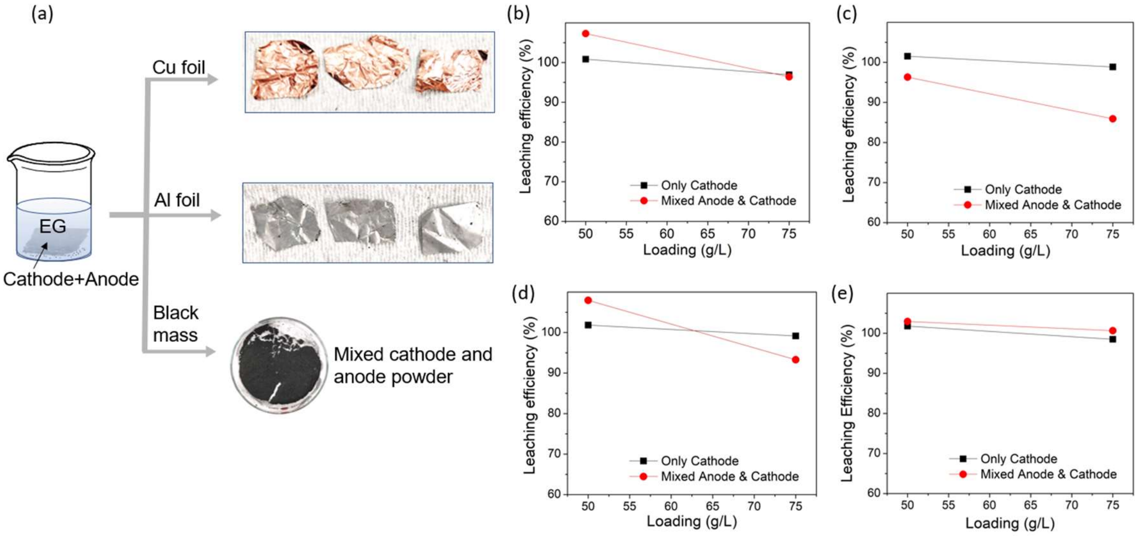

Figure 7. a) Schematic of EG-based cathode and anode direct extraction. Comparison of leaching efficiency for EG-based separated cathode with mixed cathode and anode powders at varying cathode loadings for b) Mn, c) Ni, d) Co, e) Li

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 7a 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 ºC. 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 7b-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 pre-treatment 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 pre-processing 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 hours 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 8). 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.

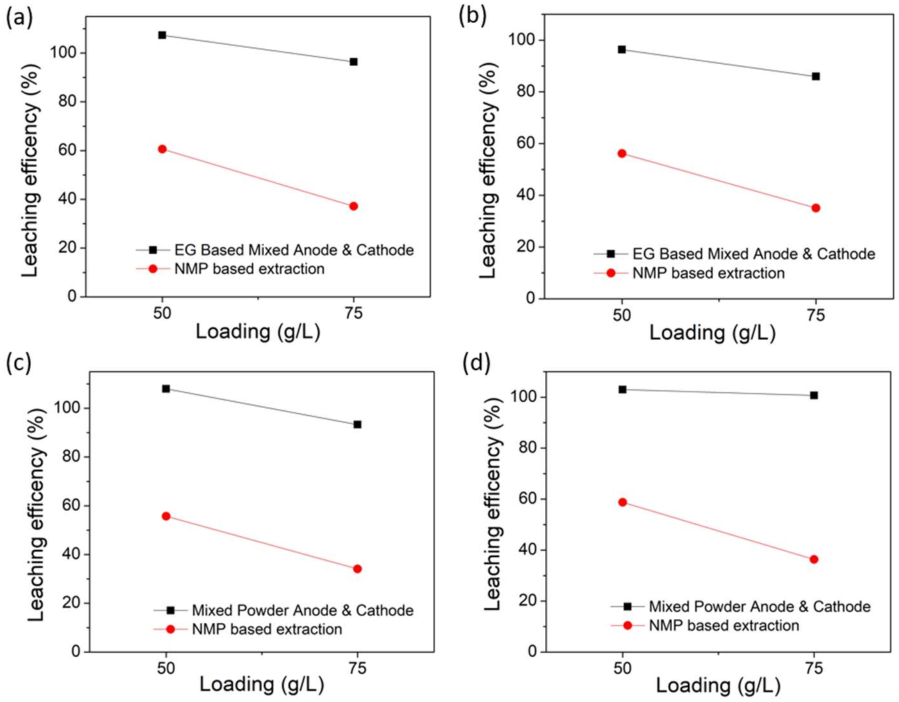

Figure 8. Comparison of leaching efficiency of EG-based mixed cathode & anode with NMP-based powder without sintering for a) Manganese b) Nickel c) Cobalt d) Lithium

2.2.5. Metal Salt Recovery

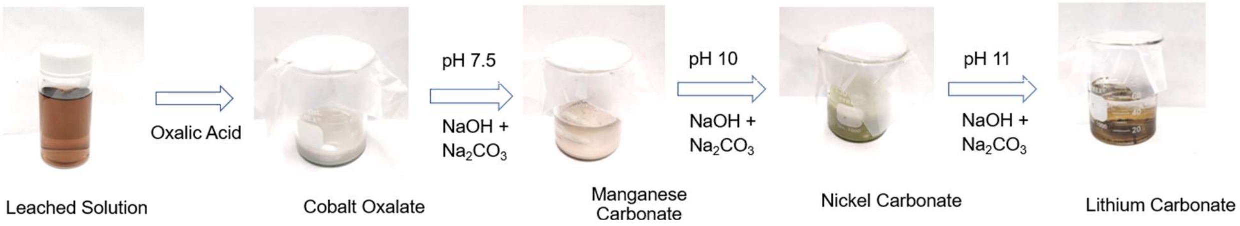

Figure 9. Schematic illustration of metal salt extraction process

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 9 shows a schematic of the salt precipitation and extraction process which is based on a method used in a previous work.[46] To the leached solution, first oxalic acid was added to recover cobalt as cobalt oxalate and it was then centrifuged and separated to re-obtain the leached solution. The pH of the solution was then increased to obtain a pH of 7.5 using a 2M 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.

Chapter 2, in full, is a reprint of the material as it appears in Advanced Energy and Sustainability Research 2021. Rose, Satchit; Xu, Panpan, Gao, Hongpeng; Li, Mingqian, Yu, Xiaolu; Zheng Chen, Wiley-VCH 2021. The thesis author was the primary investigator and author of this paper.

Chapter 3: Microwave Assisted Hydrometallurgical Recycling of Lithium-Ion Batteries

Microwaves are a type of electromagnetic radiation with frequencies at the higher end of the radio spectrum corresponding to frequencies between 300 MHz and 300 GHz. One of the most commonly used applications of microwaves are for heating which harnesses the electromagnetic properties of the waves to interact with materials. Primarily the phenomenon of heating observed is attributed to the inability of the polarization to keep up with quick changes in electric field caused by the polarization of the charges in the material. This dielectric polarization is contributed to by several individual effects which include: dipolar polarization- facilitated by a changing electric field causing realignment of dipoles of molecules, atomic polarization- the unequal distribution of charges causes a displacement of the nucleus, interfacial polarization- an effect caused by the surface limiting the distribution of electrons on it and electronic polarization- caused by the electron position changing around the nucleus.[57] From amongst these, heating is primarily attributed to dipole polarization where the constant realignment of dipoles in the molecules results in strong friction generating a large amount of heat, while interfacial polarization also plays a small part in microwave heating. On the other hand, atomic and electronic polarization contribute insignificantly to the effect due to their fast nature compared to microwave frequencies. While for solutions another vital parameter is the ion concentration, where a larger amount of ions results in more frequent collisions releasing more heat in the process and further enhancing the effect.[58] Considering this mechanism, the permittivity is considered to be the defining parameter- with it consisting of the dielectric constant and dielectric loss factor. Along with it microwave penetration depth is also considered vital to the extent of influence of microwaves on a material. Taking into account these parameters microwaves have been utilized for leaching of several metals from their ores and has been extensively demonstrating fairly high leaching efficiencies. Microwaves have been investigated for the leaching of gold, chalcopyrites (copper) as well as zinc and nickel, cobalt and manganese. [59, 60, 61, 62] Compared to conventional methods of recovery of these elements from their ores, the main differentiating factor was that high leaching efficiencies were obtained in only a fraction of the time usually required. The microwave absorbing properties of iron, cobalt, nickel and manganese ores were all seen to be quite high at elevated temperatures. [63,64] Considering that most of these elements are essential components of LIB cathodes the possibility of utilizing microwaves for leaching has been investigated in a few works. Pindar *et al.* studied the use of microwaves for recycling spent cathode material- using a specialized microwave tube furnace and with cycled graphite as the reducing agent they utilized carbothermal reduction to allow for facile leaching of cobalt and lithium. [65] Zhao *et al.* specifically investigated the microwave absorbing properties of cathode materials and at elevated temperatures demonstrated increased interactions and a boost in the dielectric constant. [66] These works demonstrate the favorable nature of cathode materials for interaction with microwaves and their efficient absorption which could potentially be further enhanced in a liquid medium. Though most prior works utilized microwave treatment for carbothermal reduction of the sample requiring specialized equipment as well as an increased complexity of the recycling methodology and a greater processing time required.

To optimize the amount of time taken for leaching, in this chapter we propose the use of a novel microwave facilitated hydrometallurgical recycling process. Though, microwave assisted recycling of LIBs has been utilized before, as mentioned in prior works the use of microwave was limited to reduction of the cathode materials prior to their leaching- still requiring a time-consuming process. [46,66] In this work we demonstrate the entire leaching process in a microwave setup with the microwaves serving as the heat source for the leaching to take place. We demonstrate fairly high leaching efficiencies of elements for high loadings of almost up to 100 g/L for a mixed $LiNi_{0.5}Mn_{0.3}Co_{0.2}$ (NMC532) and $LiMn_2O_4$ (LMO) cathode material with the leaching completed in under 10 minutes. We also expand the use of this system to other cathode chemistries and observe complete leaching in similar time frames. This method not only simplifies the process but also reduces the time required thereby lowering the overall energy consumption for the recycling loop.

3.1 Experimental methods

Materials & Reagents:

Spent LIBs were General Motor's Chevrolet Volt EV cell (20Ah), in which the cathode material composition was specified as a mixture of 66 wt.% of $LiNi_{0.5}Mn_{0.3}Co_{0.2}$ and 33wt.% $LiMn_2O_4$. The pristine LMO powder was obtained from Vendor 1. The LCO black mass mixture was obtained from Vendor 2. The pristine LFP powder was purchased from MTI Corp. All the reagents were of an analytical grade and were appropriately diluted using distilled water to lower concentrations.

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 hours to remove all residual traces of electrolyte. The cathode sheets were then washed and dried at 80 ^{o}C overnight. The sheets were cut up to have dimensions of approximately 10 cm * 8 cm and were placed in approximately 400 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 3M KOH and 0.5M 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 80ºC overnight to obtain the cathode active material. This powder was again heated at 700 ºC for 5 hours in a muffle oven and stored for future use.

Leaching of spent NCM-LMO powder:

For the study of the leaching kinetics, a total volume of 100 ml of leaching solution was used, appropriate amounts of H_2O_2 and H_2SO_4 were used and diluted to the required concentration. Fixed amount of the cycled cathode powder was added to this solution based on the mass loading. The solution with the powder was placed in the microwave setup and heated for a fixed amount of time at a power level of 90 and varying power. After leaching, the solution was removed from the microwave and then subjected to Inductively coupled plasma mass spectrometry (ICP-MS) to determine the leaching efficiency.

Leaching of spent LCO powder black mass:

For the study of the leaching kinetics, a total volume of 100 ml of leaching solution was used, appropriate amounts of H_2O_2 and H_2SO_4 were used and diluted to the required concentration. Fixed amount of LCO black mass was added to this solution based on the mass loading. The solution with the powder was placed in the microwave setup and heated for a fixed amount of time at a power level of 90 and 0.5 kW. After leaching, the solution was filtered to remove the graphite on the surface of the leached solution. The obtained solution was then subjected to Inductively coupled plasma mass spectrometry (ICP-MS) to determine the leaching efficiency.

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 20 g/L which is considered to be fully leached.

3.2 Results and Discussion

The recycling process used in the work consisted of a leaching setup where the cathode material was dissolved in a leaching solution and then heated in a microwave at a fixed power for a fixed amount of time with stirring. A common leaching solution of sulfuric acid and hydrogen peroxide was used as the previous chapter demonstrated high leaching efficiencies with it's use. Figure 10 demonstrates a schematic of the leaching process. Due to the rapid rate of heating in the microwave a condenser is used to minimize volume loss.

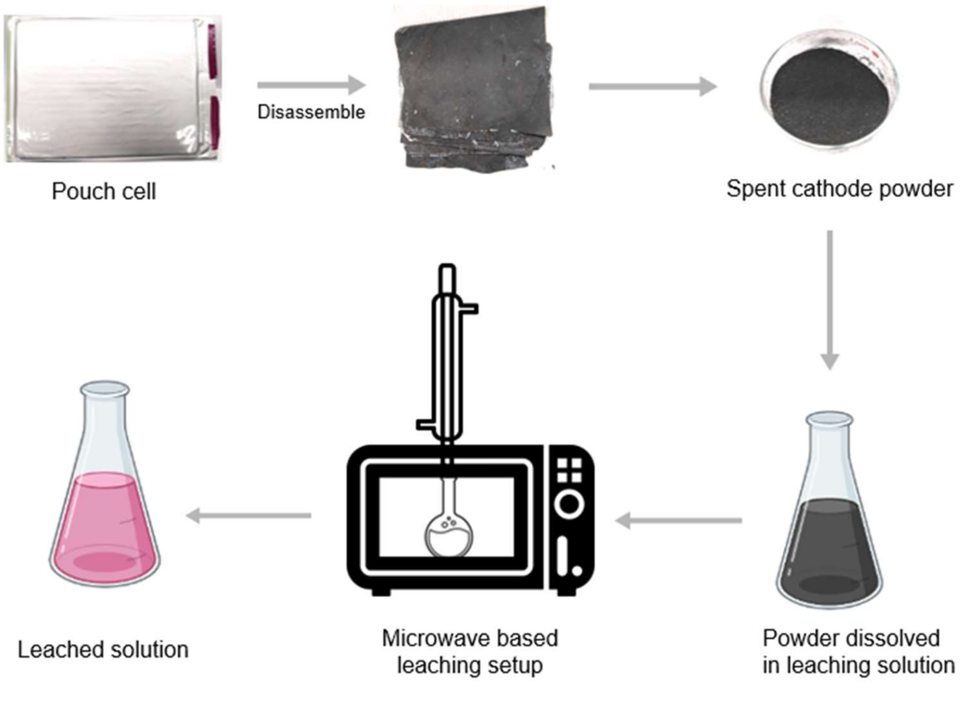

Figure 10. Schematic of the microwave-based leaching of spent LIBs

To quantify the leaching efficiency of the microwave-based process spent cathode powder- a mixture of 66% NMC 532 and 33% LMO, with a loading of 75 g/L was dispersed in the leaching solution- 2M H_2SO_4 and 2% H_2O_2 and leached using the microwave-based setup operated at a power of 0.5 kW and a power level of 90 and samples were periodically taken to study the leaching efficiency. The concentrations of the components of the leaching solution were fixed as per the optimal concentrations identified in the previous chapter. Figure 11 demonstrates the leaching of the spent mixed cathode material and we observe that as leaching time progresses the cathode material is fully leached with the color gradually becoming lighter due to the remnants of the cathode powder being further leached.

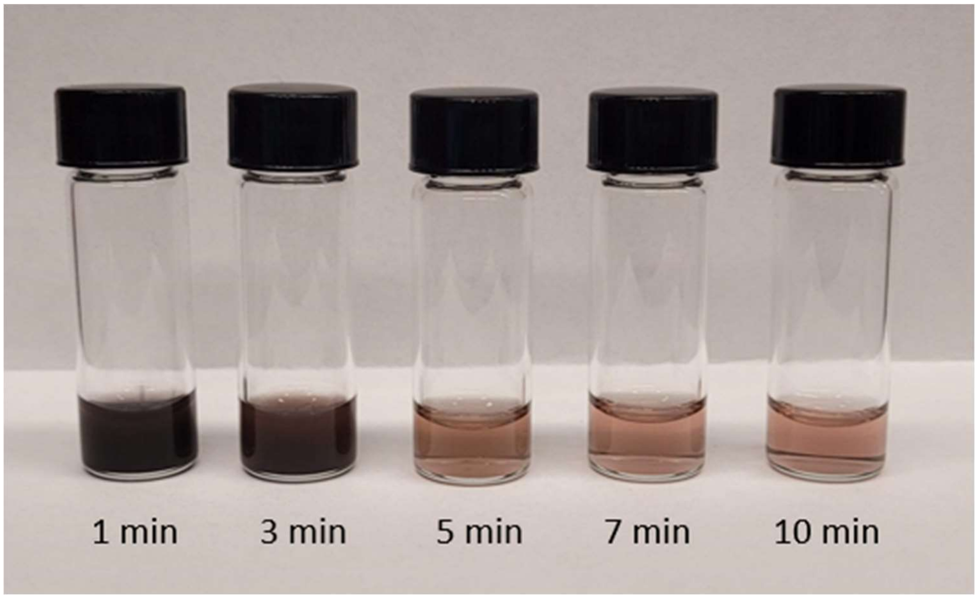

Figure 11. Time based leaching of spent cathode powder 1-10 minutes (left to right)

Figure 12 shows the time-based leaching efficiency of the process. We can see that the leaching efficiency is seen to gradually increase as the time increases from 1 to 10 minutes with a crucial increase at 5 minutes. After around 7 minutes the leaching efficiencies of all the elements is observed to be greater than 95%.

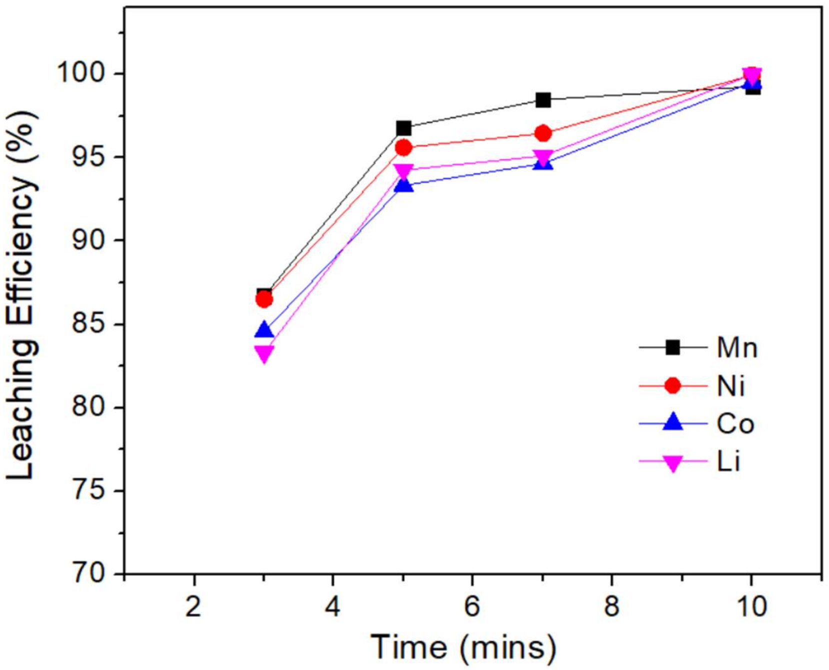

Figure 12. Variation of leaching efficiency of spent cathode powder with time

Similarly, to investigate the effect of the microwave power level on the leaching efficiency of different elements the microwave power was varied from 0.3 to 0.5 kW while the remaining parameters were kept constant- leaching solution concentration used was 2M H_2SO_4 and 2% H_2O_2 and a leaching time of 7 minutes and with a power level of 90. Figure 13 shows that an increase in the microwave power results in a tremendous increase in the leaching efficiency as the power is varied from 0.3 to 0.5 kW with efficiencies greater than 95% for all elements for the higher power.

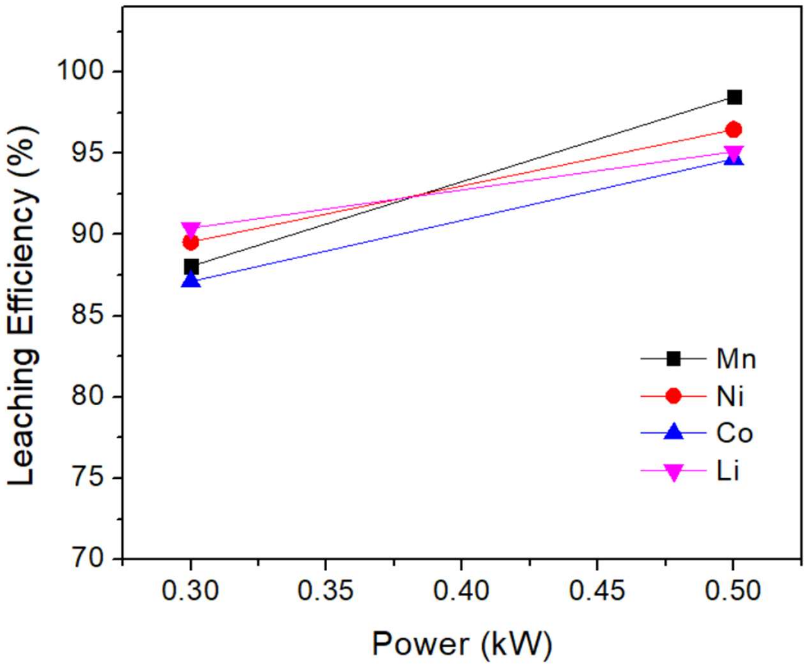

Figure 13. Variation of leaching efficiency of spent cathode powder with microwave power

To demonstrate that there is a significant reduction in leaching time for the microwave assisted process as compared to conventional heating for the leaching process we contrast the time taken to leach the cathode materials. The same set of optimized chemical concentrations and loadings were utilized in both cases and the temperature used for the conventional heating was the optimal one identified in the previous chapter. We can observe from Figure 14 that while conventional heating takes nearly 60 minutes in order to attain maximal leaching efficiencies similar efficiencies are attained in a matter of only 10 minutes using the microwave assisted leaching process significantly cutting down on the energy consumption required for the process further enhancing it’s sustainability.

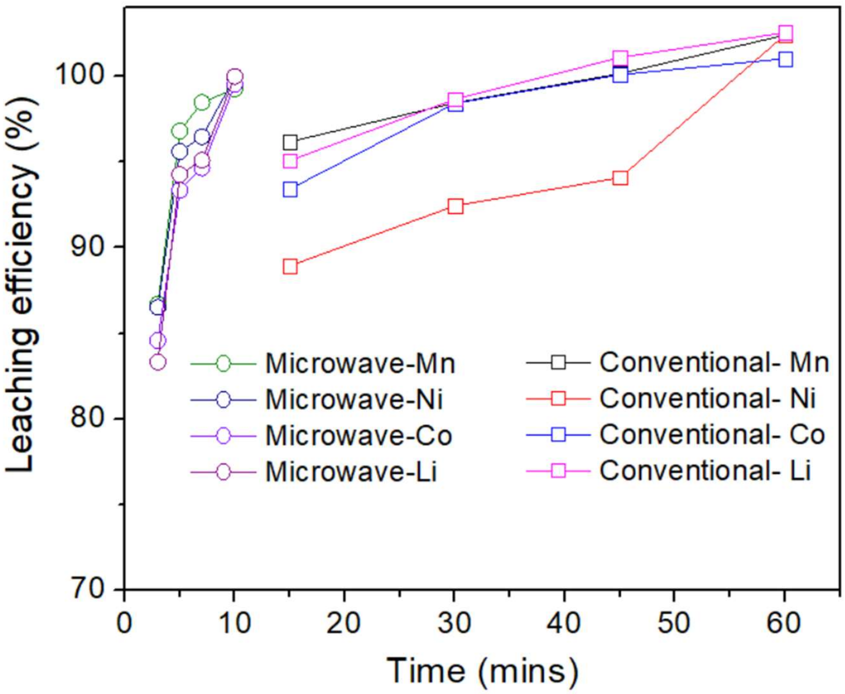

Figure 14. Comparison of leaching efficiencies for conventional and microwave assisted processes

With the same parameters the microwave-based leaching process with the same high cathode loadings was expanded to other cathode materials to show the versatility of the process. Figure 15 a) shows the leaching of pristine LFP cathode powder, after 8 minutes the solution was filtered to remove the excess remnant carbon and clear fully leached solution is observed. A spent black mass mixture of LCO and graphite was leached using the same process and is shown to be fully leached in Figure 15 (b) after filtration of the graphite on the surface. The solution was seen to be fully leached in just 6 minutes indicating the practicality of the method for industrial use. Similarly, to demonstrate the effectiveness of the process for spinel type structures, pristine LMO cathode material was leached. Figure 15 (c) shows the leached solution and the leaching was completed in just 2 minutes and no residual cathode powder was observed indicating the ease of element extraction from spinel type cathode structures.

Figure 15. Fully leached solutions of other cathode materials after microwave-based leaching of a) LFP b) LCO c) LMO

Conclusion

In summary, in this work we demonstrated the impact of the use of EG as a cathode separation agent on the overall leaching efficiency of LIB cathode materials. Compared to prior works significantly high cathode powder loadings of up to 100 g/L were used thereby allowing for a more efficient use of the leaching solution. The boost in leaching efficiency was shown to be caused solely by the use of EG by comparing the efficiencies with that of powder obtained from a conventional NMP based cathode separation method demonstrating that the use of EG provides reducing moieties to the cathode powder, easing the reduction of elements and enhancing the leaching process. The scope of the process was further expanded by leaching a cathode and anode mixture and showing equally high leaching efficiencies thereby reducing the pre-treatment required. The metal salts were then recovered using a simple salt precipitation process that avoids the use of expensive salt separation agents commonly utilized.

To further improve the process and minimize the leaching time expended, the leaching is conducted in a microwave-based setup. High leaching efficiencies are demonstrated with leaching times as short as 7 minutes even at loadings as high as 75 g/L. The leaching process parameters were then optimized and the universal applicability of the microwave-based process was shown by leaching a number of different cathode materials demonstrating leaching capability in short time frames. In the future, further optimization of parameters and thorough investigation of the impact of microwaves on the leaching process can be investigated. Also, the salt extraction route can be modified in future works to allow for the direct synthesis of high- capacity cathode materials from the leached solution. By improving the scalability of the EG based and microwave process we anticipate that our work can enable a greener and more sustainable industrial recycling process.

Chapter 3 is coauthored with Yu, Xiaolu; Gao, Hongpeng and Chen, Zheng. The thesis author was the primary author of this chapter.

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