

Article

Efficient Leaching of Metal Ions from Spent Li-Ion Battery Combined Electrode Coatings Using Hydroxy Acid Mixtures and Regeneration of Lithium Nickel Manganese Cobalt Oxide

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Abstract: Extensive use of Li-ion batteries in electric vehicles, electronics, and other energy storage applications has resulted in a need to recycle valuable metals Li, Mn, Ni, and Co in these devices. In this work, an aqueous mixture of glycolic and lactic acid is shown as an excellent leaching agent to recover these critical metals from spent Li-ion laptop batteries combined with cathode and anode coatings without adding hydrogen peroxide or other reducing agents. An aqueous acid mixture of 0.15 M in glycolic and 0.35 M in lactic acid showed the highest leaching efficiencies of 100, 100, 100, and 89% for Li, Ni, Mn, and Co, respectively, in an experiment at 120 °C for 6 h. Subsequently, the chelate solution was evaporated to give a mixed metal-hydroxy acid chelate gel. Pyrolysis of the dried chelate gel at 800 °C for 15 h could be used to burn off hydroxy acids, regenerating lithium nickel manganese cobalt oxide, and the novel method presented to avoid the precipitation of metals as hydroxide or carbonates. The Li, Ni, Mn, and Co ratio of regenerated lithium nickel manganese cobalt oxide is comparable to this metal ratio in pyrolyzed electrode coating and showed similar powder X-ray diffractograms, suggesting the suitability of α -hydroxy carboxylic acid mixtures as leaching agents and ligands in regeneration of mixed metal oxide via pyrolysis of the dried chelate gel.

Keywords: lithium nickel manganese cobalt oxide; glycolic acid; lactic acid; leaching; chelate gel; pyrolysis



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1. Introduction

Electrification of transportation and transition to renewable solar and wind electrical energy generation are major steps in decarbonization efforts to mitigate climate change. Energy storage using batteries is a key component in this process, and Li-ion batteries (LiBs) are at the forefront of this revolution owing to their high energy density and efficiency. Battery chemistry, capacity, charge-discharge characteristics, safety, and cost of Li-ion batteries can be different depending on the type of energy storage device. Handheld and smaller portable electronic devices like cell phones are mostly equipped with polymer gel-type lithium-ion batteries since the weight of batteries is a significantly important factor. Liquid electrolytes are common in most batteries, whereas polymer gels are used in lightweight batteries in small mobile devices where the weight is critically important. These batteries generally use lithium cobalt oxide (LiCoO₂) as cathode electrode coating material, together with a graphite or lithiated graphite as the anode. Furthermore, these mobile device batteries can offer high energy density. However, these batteries offer a shorter life span in comparison to Li-ion batteries used in automobiles [1,2]. Lithium manganese oxides such as LiMn₂O₄ spinel or Li₂MnO₃-based Li-rich, layered materials, lithium iron phosphate (LiFePO₄), and lithium nickel manganese cobalt oxide (LiNi_xMn_yCo_zO₂) commonly abbreviated as LiNMC are known to offer relatively longer battery lives as

much as 8–10 years and known for high discharging rates as well. Liquid electrolytes such as lithium hexafluorophosphate are commonly used in these heavy-duty batteries used in electric automobiles, power tools, medical equipment, household appliances, and large energy storage devices such as power walls. Additionally, a very wide range of lithium metal oxide complexes combined with other metals such as Fe, Ni, Co, and Mn are presently used in the preparation of cathode electrode coatings. The active metal oxide or their mixtures are generally found with graphite used as the conductor and binders such as polyvinylidene fluoride and styrene–butadiene copolymer. The chemical formulas and elemental percentage compositions of a selected group of current and widely used cathode active materials are shown in Table 1.

Table 1. Chemical formulas and elemental percentage compositions of some currently used common Li-ion battery cathode materials.

Cathode Material	Elemental Composition (<i>w/w</i> %)				Reference
	Li	Ni	Mn	Co	
LiCoO ₂	7.03	-	-	59.55	[3]
LiMnO ₄	3.99	-	58.39	-	[3]
LiNi _{0.3} Mn _{0.3} Co _{0.3} O ₂	2.52	6.76	6.81	7.01	[4]
LiNi _{0.3} Mn _{0.3} Co _{0.3} O ₂	6.15	18.32	17.57	18.65	[5]
LiNi _{0.5} Mn _{0.3} Co _{0.2} O ₂	6.34	26.75	15.34	10.77	[6]
LiNi _{0.6} Mn _{0.2} Co _{0.2} O ₂	6.64	35.1	11.2	12.1	[7]
LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	7.36	46.01	5.40	6.28	[8]

The lifespan of LiBs is another important factor and generally depends on the application. Batteries used in electronic devices such as cell phones and laptop computers are expected to perform for 2–3 years, whereas in electric vehicles (EVs), the batteries are expected to last 8–10 years [9]. However, the widespread usage of LiBs unavoidably leads to a rapid increase in the quantity of end-of-life Li-ion batteries [10–12]. The evaluation of worldwide accumulation of used Li-ion batteries is a difficult task, and one estimate gives a value of 1.7 million tons of used batteries and a recycling market of approximately US \$ 1.7 B by 2035 [13–15]. These data indicate that discarded Li-ion batteries are among the increasing wastes that contain high concentrations of valuable critical metals: Li, Mn, Ni, and Co, found only in narrow geographical regions on Earth [11]. Furthermore, transition metal concentrations, particularly Mn, Ni, and Co used in Li-ion batteries, can exceed the critical toxicity limits set by environmental protection agencies, posing a substantial threat to the environment [16]. In order to curtail the harmful environmental effects of the direct disposal of used lithium-ion batteries and also to recover valued metals such as Li, Mn, Ni, and Co from used batteries, a range of recycling and end-of-life management approaches are currently in development. This wide variety of technologies is grounded on pyrolysis, hydro-metallurgical processes, biotechnology methods, and enzymatic techniques, as well as combinations of these methods. There are certain advantages and disadvantages to all these technologies. For instance, pyro-metallurgical processes usually do not require pre-treatment and generally avoid pre-processing; however, they mostly result in alloys, which will need complex post-separations using hydrometallurgical or other methods [17]. In addition, pyro-metallurgical processes require high energy input and possible environmental pollution due to the discharge of toxic vapors and gasses, and this could be a major concern in large-scale pyro-metallurgy [17].

Therefore, hydrometallurgical methods involving leaching with mineral acids, frequently with oxidizing or reducing agents, have attracted wider attention in recent years [18–20]. Compared to the pyro-metallurgical approach, hydrometallurgical methods are more environmentally friendly and energy-efficient; nevertheless, the separation of individual metals requires complex precipitation or solvent extraction methods [21,22]. Strong acids such as sulfuric, nitric, or hydrochloric acid are generally used as the main leaching agent in these hydro-metallurgical metal recovery methods, and disposal of large quantities of strong acids is another environmental concern in the scale-up of the mineral acid process.

As a solution to this issue, in recent years, a number of research groups have studied the use of organic acids with weakly acidic character and favorable biodegradability profiles as an alternative to mineral acids. Naturally occurring mono, di, and tricarboxylic acids are often used, and they include gluconic, lactic, succinic, malic, maleic, oxalic, tartaric, and citric acids [23–25]. These acids are frequently used together with reducing reagents such as hydrogen peroxide, iron, sodium sulfite, and sulfur dioxide. In addition, organic acids or carbohydrate compounds like glucose, ascorbic acid, sucrose, cellulose, oxalic acid, or molasses have also been tested to enhance the effect of acid leaching of metal ions from spent Li-ion battery materials [26–28]. However, there is little understanding of the underlying principles and the role of these additional reducing or oxidizing agents, as well as the organic acids tested in the leaching of critical metals from used battery materials. For instance, there is limited information on selectivity in the chelation of different organic acids towards Li, Ni, Mn, and Co cations and applications of complex stabilities to achieve selective extractions [29]. For example, the use of a mixture of lactic acid and hydrogen peroxide was reported by Li and coworkers [30]. Where they reported 97.7, 98.2, 98.9, and 98.4% leaching efficiencies for Li, Ni, Co, and Mn, respectively, using 1.5 mol L^{-1} lactic acid with 0.5 vol% hydrogen peroxide, 20 g L^{-1} solid/liquid ratio at $70 \text{ }^\circ\text{C}$ [30]. In attempts to regenerate the original mixed metal oxide, Li and co-workers adjusted the concentrations of Li, Ni, Co, and Mn to 3.05:1:1:1 by adding acetate salts of Li, Ni, Co, and Mn to the leachate solution. Next, an ammonia solution was added before drying the solution, heating at $450 \text{ }^\circ\text{C}$ for 5 h, followed by $900 \text{ }^\circ\text{C}$ for 12 h to regenerate lithium nickel manganese cobalt oxide [30]. In another example, Ning and co-workers have reported >97% leaching of Li, Ni, Mn, and Co using 1 M aqueous DL-malic acid and 4% hydrogen peroxide mixture under ultra-sonication at $80 \text{ }^\circ\text{C}$ [7]. Furthermore, they regenerated the cathode material after adding Ni, Mn, and Co in the form of their acetates and precipitation as carbonate by adding 0.6 M aqueous Na_2CO_3 , followed by pyrolysis at $450 \text{ }^\circ\text{C}$ for 5 h and $800 \text{ }^\circ\text{C}$, 15 h [7]. In a more recent example, Sidiq and co-workers claimed that 95% leaching efficiencies could be achieved using DL-malic acid and D-glucose as the reducing agent [23]. Then, the cathode material was regenerated by the addition of lithium acetate, precipitation as oxalate by the addition of oxalic acid, followed by pyrolysis at $900 \text{ }^\circ\text{C}$ [23]. The use of common hydroxy polycarboxylic acid (citric acid) without an oxidizing agent for leaching metals from simpler mixed metal oxides such as lithium cobalt oxide and lithium nickel cobalt oxide is known [31,32]. In the lithium cobalt oxide example, Martins and co-workers have reported quantitative leachings of both Li and Co from LiCoO_2 battery material by using 1.0 M aqueous citric acid without any additional reagents [31]. Similarly, de Castro and co-workers used an aqueous solution of citric acid without other reagents and reported over 80% leaching for Li, Ni, and Co at $90 \text{ }^\circ\text{C}$ [32].

We have been studying the catalytic activities of the lithium nickel manganese cobalt oxide with the general formula $\text{Li}_a\text{Ni}_b\text{Mn}_c\text{Co}_d\text{O}_e$ derived from spent Li-ion battery waste for oxidation of sugars as well as biomass-derived furans for producing value-added products such as glycolic acid in recent years [33,34]. In addition, we have reported the use of lithium nickel manganese cobalt oxide as a catalyst for decarboxylative dimerization of levulinic acid in upgrading this biomass-derived carboxylic acid [35]. While attempting to oxidize glucose to gluconic acid using battery waste LiNMC/graphite catalyst, we have observed a facile oxidation of glucose to a mixture of carboxylic acids, including some hydroxy acids and effortless leaching of Li, Ni, Mn, and Co metal ions in LiB electrode coating material into aqueous medium under mild conditions [33]. This accidental discovery motivated us to study mixtures of inexpensive α -hydroxy acids as chelating agents and without additional reagents for leaching out Li, Ni, Mn, and Co from spent Li-ion battery waste for the recovery of critical metals. Combined cathode and anode coating used in the current work was collected from 18,650 Li-ion cells in a spent DELL 1525 laptop battery, as shown in Figure 1. In this publication, we report the use of lactic, glycolic acid mixtures for leaching out Li, Ni, Mn, and Co as well as facile regeneration of lithium nickel manganese

cobalt oxide through pyrolysis of chelate sol-gel formed with these α -hydroxy carboxylic acids without the use of additional precipitation reagents as shown in Figure 2.

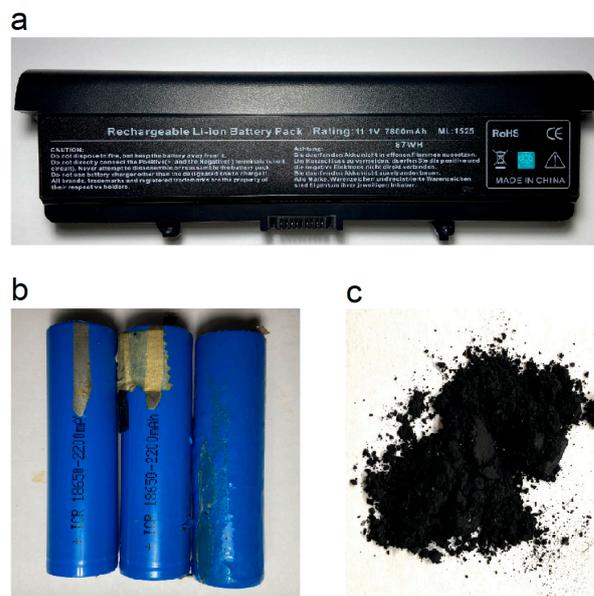


Figure 1. (a) Spent DELL 1525, 87 Wh, 11.1 V laptop battery; (b) 18,650 Li-ion cells; (c) combined cathode and anode coating collected from 18,650 Li-ion cells after the removal of electrolytes and binders by pyrolysis at 700 °C (LiBBM-700).

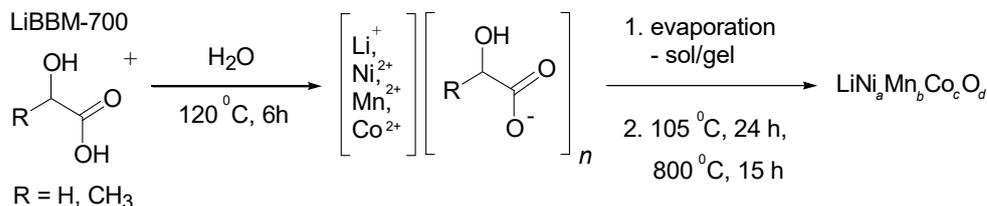


Figure 2. Leaching of Li, Ni, Mn, and Co in pyrolyzed spent Li-ion battery electrode coating black material (LiBBM-700) and recovery of lithium nickel manganese cobalt oxide ($\text{LiNi}_a\text{Mn}_b\text{Co}_c\text{O}_d$) by pyrolysis of metal-hydroxy carboxylic acid chelate gel.

2. Experimental

2.1. Materials and Instrumentation

Glycolic acid (99.9%), lactic acid (99.9%), nitric acid (99.9%), and hydrochloric acid (99.9%) were obtained from Thermo Fischer Scientific, Waltham, MA, USA. A 4-year-old, 87 Wh, 11.1 V, spent DELL 1525 laptop battery was used as the source for the electrode coating material. Cathode and anode coatings of aluminum and copper foils were removed by sonication using 130 W in Sonics Vibro-Cell sonicator on a low power setting at 30 W. All pyrolysis experiments were carried out in alumina crucibles using a Thermolyne 1400 Benchtop 2.1 L, muffle furnace. Metal ion leaching experiments using aqueous organic acids were carried out in 100–250 mL reaction kettles with Teflon inner sleeves and stainless-steel jackets. These high-pressure reaction kettles were purchased from Lonsino Medical Product Suppliers Co. Ltd., Lianyungang, China. The high-pressure reactors were heated using a preheated microprocessor-controlled WU-52402-91 convection oven with $\pm 1^\circ\text{C}$ accuracy obtained from Cole-Palmer, Vernon Hills, IL, USA. JEOL JSM-6010LA instrument operated through InTouchScope software (version 3.2) was used for energy dispersive X-ray spectroscopy (EDX) analyses. The backscattered electron images were collected at 10 kV accelerating voltage and at $\sim 90\ \mu\text{A}$ load current. The working distance was 9 mm. EDS spectra of the samples were collected at $500\times$ magnification. The analysis area was approximately $0.15\ \text{mm}^2$ ($110\ \mu\text{m} \times 135\ \mu\text{m}$) for all samples. Scanning

electron microscopy (SEM) was carried out using a FEI Quanta 400 ESEM instrument. Powder X-ray diffractograms of catalysts were collected on a Bruker D8 Endeavor X-ray spectrometer (Billerica, MA, USA) with a 1 kW Cu X-ray tube as an X-ray source, operated at 25 mA, 40 kV, wavelength of 1.54060 Å, and scan time of 60 min. Data collection was automated by employing the COMMANDER program and a DQL file. Data were analyzed by the program EVA. The Li, Ni, Mn, and Co concentrations in leachate solutions were determined using a Varian SpectraAA 220FS atomic absorption spectrometer (Palo Alto, CA, USA) and Li and Ni and Mn and Co hollow cathode lamps. The solutions were acidified with 0.10 M HCl before analysis, and standard curves were prepared for each metal using a 0.10 M HCl acidified set of five standards, each of which was used to calculate metal ion concentrations in test solutions.

2.2. Analysis Procedure Using Atomic Absorption Spectroscopy

The Li, Ni, Mn, and Co concentrations in leachate solutions were determined using a Varian SpectraAA 220FS atomic absorption spectrometer with Li and combined Ni, Mn, and Co hollow cathode lamps. The solutions were acidified with 0.10 M HCl before analysis, and a standard curve was prepared for each metal using a 0.10 M HCl acidified set of five standards, each of which was used to calculate metal ion concentrations in test solutions. Airflow, 2 Lmin⁻¹; acetylene flow, 13.5 Lmin⁻¹; lamp current, 5 mA; slit height, normal; slight width, 0.5 nm for Li and 0.2 nm for Ni, Mn, and Co. Wavelengths: Li 670.8, Ni 232.0, Mn 279.5, and Co 240.7 nm.

2.3. Collection of Lithium-Ion Battery Black Material (LiBBM), Preparation of Pyrolyzed Product (LiBBM-700), and Characterization

A used DELL 1525 laptop battery (87 Wh, 11.1 V) was completely discharged by immersing in 10% aq. sodium chloride solution for 6 days at 23 °C. The outer covering was removed to collect nine 18,650 Li-ion cells, and these cells were opened by cutting through the metal casing to collect copper anode and aluminum cathode foils with black coatings. These foils were placed in a beaker with deionized water to cover the foils and sonicated at 30 W in Sonics Vibro-Cell sonicator for 4 h at 23 °C. Copper and aluminum foils were removed, and combined cathode and anode coating black powder was collected by filtration and washed three times with deionized water and air dried for 2 days to give 44 g of combined Li-ion battery black mass (LiBBM). Next, LiBBM was pyrolyzed at 700 °C in air for 4 h, using an alumina crucible in a Muffle furnace. The cooled electrode material was powdered using a Micro-Mill grinder and sieved through a number 25 mesh to give 36 g of pyrolyzed lithium-ion battery black mass named LiBBM-700, which was stored in air-tight glass bottles until used. The pyrolyzed electrode coating LiBBM-700 was characterized by using SEM, EDX, and powder X-ray spectroscopy, and these spectrographs are shown in Figures 3a, 3b, and 4a, respectively.

2.4. Composition of LiBBM-700 by Analysis of Li, Ni, Mn, and Co

LiBBM-700 (100 mg) was mixed with 2.0 mL of aqua regia (HNO₃:HCl 1:3 mole mixture) and heated at 100 °C for 6 h to digest Li, Ni, Mn, and Co in the black powder, then diluted with 100 mL of deionized water, filtered through a glass sinter funnel to remove the graphite. The graphite was repeatedly washed with deionized water (3 × 25 mL), and washings were combined with filtrate. The graphite collected was dried in an oven at 105 °C for 8 h to determine the graphite content in LiBBM-700. The combined leachate solution was acidified to 0.10 M HCl with concentrated HCl and analyzed for Li, Ni, Mn, and Co using atomic absorption spectroscopy as described above. The oxygen *w/w* percentage was determined by subtracting the weight percentages of metals and graphite carbon from the weight of the LiBBM-700 sample used in the analysis. The Li, Ni, Mn, Co, O, and C (*w/w*)% composition of LiBBM-700 and the calculated empirical molecular formula of lithium nickel manganese cobalt oxide in LiBBM-700 are shown in Table 2.

Table 2. Elemental compositions and calculated empirical formulas of LiNMC in LiBBM-700 prepared from laptop battery combined electrode coatings and regenerated LiNMC from Table 3, Entry 11 leaching solution.

Sample	Elemental Composition (w/w)%						Empirical Formula
	Li	Ni	Mn	Co	O	C	
LiNMC in LiBBM-700	13.33	3.76	2.44	12.33	11.28	56.86	LiNi _{0.03} Mn _{0.02} Co _{0.11} O _{0.35}
Regenerated LiNMC (Table 3, Entry 11)	32.60	9.06	5.58	29.93	22.83	-	LiNi _{0.03} Mn _{0.02} Co _{0.11} O _{0.30}

Table 3. Leaching efficiencies of Li, Ni, Mn, and Co in aqueous lactic and glycolic acid solutions and their mixtures, weight of LiBBM-700 to leaching solution volume ratios, and glycolic (GA) and lactic (LA) concentrations. All leaching experiments were carried out at 120 °C, 6 h, in high-pressure reactors. Average of duplicate experiments.

Entry	LiBBM-700 (g)/Leaching Solution (mL)	[GA] mol L ⁻¹	[LA] mol L ⁻¹	Leaching Efficiency of Metal Ions (%)			
				Li	Ni	Mn	Co
1	1:100	0.00	0.25	69	54	34	34
2	1:100	0.05	0.20	98	100	100	87
3	1:100	0.075	0.175	100	86	82	69
4	1:100	0.25	0.00	73	46	33	34
5	1:100	0.00	0.10	99	100	100	85
6	1:100	0.02	0.08	93	100	100	91
7	1:100	0.03	0.07	98	100	100	88
8	1:100	0.10	0.00	92	100	100	74
9	1:100	0.00	0.50	100	97	100	81
10	1:100	0.10	0.40	100	100	100	85
11	1:100	0.15	0.35	100	100	100	89
12	1:100	0.20	0.30	100	84	89	65
13	1:100	0.25	0.25	100	100	100	83
14	1:20	0.25	0.25	67	72	84	74
15	1:100	0.30	0.20	100	89	97	78
16	1:100	0.50	0.00	100	100	100	73

2.5. General Procedure for Leaching Li, Ni, Mn, and Co from LiBBM-700 Using Aqueous Hydroxy Acid Solutions

LiBBM-700 (100–500 mg) was suspended in 20–100 mL aqueous solutions of glycolic and lactic acids or a mixture in a stainless steel solvothermal reaction kettle with a Teflon inner sleeve and heated at 120 ± 1 °C for 6 h in a convection oven. The kettle was cooled to room temperature, and the contents were filtered through a glass sinter funnel to remove the graphite. The graphite collected was washed with deionized water (3 × 25 mL), and washings were combined with filtrate. The combined leachate solution was acidified to 0.10 M HCl with concentrated HCl and analyzed for Li, Ni, Mn, and Co using atomic absorption spectroscopy as described above. Leaching Li, Ni, Mn, and Co data to aqueous lactic and glycolic acid solutions and their mixtures were calculated using the following formula:

$$\text{leaching efficiency of a metal (\%)} = \frac{\text{Weight \% of metal leached into aq. hydroxy acid } \left(\frac{w}{w}\right) \%}{\text{Weight \% of metal digested into aqua regia } \left(\frac{w}{w}\right) \%} \times 100\% \quad (1)$$

The concentrations of lactic and glycolic acid and mixtures used, LiBBM-700 to liquid ratios, and Li, Ni, Mn, and Co leaching efficiency data in using aqueous lactic and glycolic acid solutions and their mixtures are shown in Table 3.

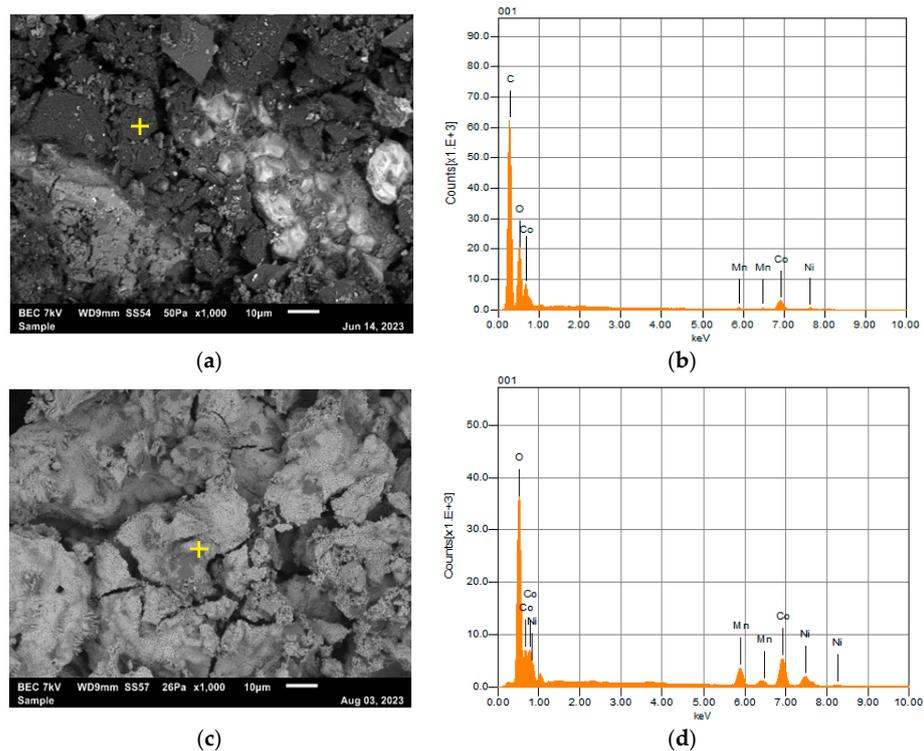


Figure 3. (a) Scanning electron microscopy (SEM) image of LiBBM-700; (b) energy dispersive X-ray spectroscopy (EDX) of LiBBM-700; (c) SEM image of LiNMC regenerated from hydroxy carboxylic acid chelate in entry 11, Table 3; (d) EDX of LiNMC regenerated from hydroxy acid chelate in entry 11, Table 3.

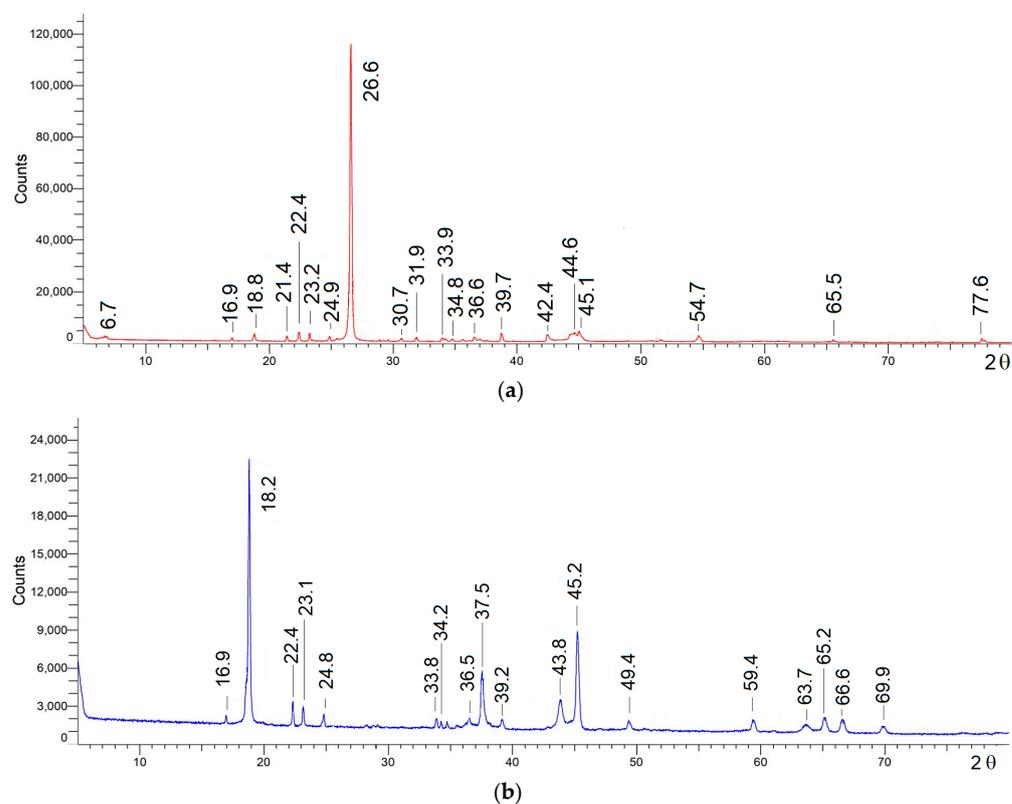


Figure 4. (a) Powder X-ray diffractogram of LiBBM-700; (b) powder X-ray diffractogram of LiNMC regenerated from hydroxy acid chelate solution in entry 11, Table 3.

2.6. Regeneration of Lithium Nickel Manganese Cobalt Oxide through Pyrolysis of Chelate Gel

Li, Ni, Mn, and Co leaching solution from entry 11 in Table 3 was selected for regeneration of lithium nickel manganese cobalt oxide on the basis of high leaching efficiency found in using 0.15 mol L^{-1} GA and 0.35 mol L^{-1} LA mixture. The clear solution obtained after filtration of graphite was evaporated in a steam bath for 3 h to form a gel. The gel was further dried at $105 \text{ }^\circ\text{C}$ for 24 h in an oven and, after that, pyrolyzed at $800 \text{ }^\circ\text{C}$ in an alumina crucible for 15 h to give regenerated lithium nickel manganese cobalt oxide as a black powder, as shown in Figure 5.



Figure 5. LiNMC regenerated from hydroxy carboxylic acid chelate solution in entry 11, Table 3, with formula $\text{LiNi}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.30}$ and alumina crucible used in $800 \text{ }^\circ\text{C}$ pyrolysis.

2.7. Analysis of Li, Ni, Mn, and Co in Regenerated Lithium Nickel Manganese Cobalt Oxide

Regenerated lithium nickel manganese cobalt oxide (100 mg) was mixed with 2.0 mL of aqua regia ($\text{HNO}_3:\text{HCl}$ 1:3 mole mixture) and heated at $100 \text{ }^\circ\text{C}$ for 6 h. to completely dissolve LiNMC, then diluted with 100 mL of deionized water, filtered through a glass sinter funnel to give a clear solution, acidified to 0.10 M with concentrated HCl and analyzed for Li, Ni, Mn, and Co using atomic absorption spectroscopy as described above.

3. Results and Discussion

3.1. Collection and Preparation of Pyrolyzed Lithium-Ion Battery Black Material (LiBBM-700) and Characterization

LiBBM-700 electrode coating material used in the leaching experiments was prepared by pyrolysis ($700 \text{ }^\circ\text{C}$) of combined cathode and anode black powder collected from aluminum and copper electrode foils in nine completely discharged Li-ion battery cells. An approximately 10 mg sample of combined anode and cathode coating powder collected was first subjected to thermogravimetric analysis (TGA) to determine the preparative scale pyrolysis temperature. This experiment showed that pyrolysis in the air at $700 \text{ }^\circ\text{C}$ could be used to remove binders like polyvinylidene fluoride, styrene-butadiene rubber, polytetrafluoroethylene, and carboxymethyl cellulose as well as residual electrolytes from combined electrode coating. Therefore, the combined electrode coating was pyrolyzed at $700 \text{ }^\circ\text{C}$ for 30 min. before Li, Ni, Mn, and Co leaching experiments. The LiBBM-700 was characterized before leaching using SEM, EDX, and powder X-ray spectroscopy, and these spectrographs are shown in Figures 3 and 4. The x1000 SEM image of LiBBM-700 in Figure 3a shows 10–20 mm non-homogeneous lumps, whereas in energy dispersive X-ray spectroscopy (EDX) analysis of LiBBM-700 in Figure 3b shows the presence of C, O, Li, Ni, Mn, and Co in the sample. The elemental composition of LiBBM-700 was determined by weighing the graphite carbon separated and quantitative analysis of Li, Ni, Mn, and Co in aqua regia digested sample by atomic absorption spectroscopy as described in the experimental section, and the results are shown as the first entry in Table 2. The empirical molecular formula of lithium nickel manganese cobalt oxide in LiBBM-700 was determined

as $\text{Li}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.35}$, as shown in the first entry in Table 2. The powder X-ray spectrograph of LiBBM-700 is in Figure 4a. The strong peaks at $2\theta = 26.6^\circ$ and smaller peaks at 44.6° are due to the major component graphite carbon in the sample; the weaker peaks are from the minor component Li, Ni, Mn, and Co mixed metal oxide [36].

3.2. Leaching Li, Ni, Mn, and Co from LiBBM-700 Using Aqueous Hydroxy Acid Solutions

Leaching Li, Ni, Mn, and Co from LiBBM-700 was tested using aqueous solutions of glycolic and lactic acids and their mixtures of varying concentrations at different solid/liquid ratios. The liquid phase was filtered off after the leaching, and Li, Ni, Mn, and Co concentrations in the liquid phase were determined by using atomic absorption spectroscopy (AA). The percentage of leaching of each metal was determined using Equation (1) in the experimental section, assuming 100% dissolution of metals under aqua regia digestions described for the determination of metal content in LiBBM-700. The percentages of leaching of Li, Ni, Mn, and Co to aqueous lactic and glycolic acid solutions and their mixtures under variable conditions are shown in Table 3. Initial tests using low concentrations of lactic acid only resulted in low leaching efficiencies for all metal ions, as shown in entry 1, where only 69, 54, 34 and 34% leaching of Li, Ni, Mn, and Co, respectively, were observed in 0.25 mol L^{-1} aqueous lactic acid medium using 1:100 LiBBM (g)/leaching solution (mL) solid to liquid ratio at 120°C , for 6 h. However, later experiments using lactic acid and glycolic acid mixtures and higher concentrations of these hydroxy acids resulted in significant improvements in leaching efficiencies. The highest leaching efficiency of 100, 100, 100 and 89% leaching of Li, Ni, Mn, and Co, respectively, were observed in using an aqueous mixture of 0.15 mol L^{-1} glycolic and 0.35 mol L^{-1} lactic acid and 1:100 (g/mL) solid to liquid ratio as shown in entry 11 of Table 3. Furthermore, this hydroxy carboxylic acid composition was selected for further experiments on the regeneration of lithium nickel manganese cobalt oxide from leachate solution by pyrolysis method due to the excellent extraction ability of all four metals from LiBBM-700. In addition, it is interesting to note that the use of higher loading of LiBBM 1:20 (g/mL) solid to liquid ratio resulted in a lowering of leaching, as demonstrated in entry 14.

3.3. Regeneration of Lithium Nickel Manganese Cobalt Oxide Using Leachate Solution from Entry 11 in Table 3 and Comparison with Lithium Nickel Manganese Cobalt Oxide in LiBBM-700

Evaporation of water from Li, Ni, Mn, and Co leachate solution from entry 11 in Table 3 on a steam bath resulted in the formation of pink-purple sol-gel of the mixed metal-hydroxy acid chelate. This gel was first dehydrated in an oven and then transferred to an alumina crucible for pyrolysis. The pyrolysis and sintering at 800°C resulted in black powder, as shown in Figure 5. Next, the regenerated lithium nickel manganese cobalt oxide was analyzed for Li, Ni, Mn, and Co using atomic absorption spectroscopy after digestion with aqua regia, as described in the experimental section. The Li, Ni, Mn, Co, and O (*w/w*)% composition of regenerated lithium nickel manganese cobalt oxide is shown in the second entry of Table 2. The oxygen content of the regenerated mixed metal oxide was calculated by subtraction of the total metal weight from the regenerated lithium nickel manganese cobalt oxide initial sample weight used for the analysis. Furthermore, the empirical formula of regenerated lithium nickel manganese cobalt oxide could be calculated as $\text{LiNi}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.30}$, as shown in entry 2 of Table 2. It is noteworthy to see that this formula is comparable to the empirical formula of lithium nickel manganese cobalt oxide in original LiBBM-700, $\text{LiNi}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.35}$. The SEM image of LiNMC regenerated from hydroxy acid chelate in entry 11, Table 2, is shown in Figure 3c. This image shows 10–25 mm irregular, homogeneous lumps with surface perforations. Furthermore, it is interesting to note that this SEM image of regenerated LiNMC (Figure 3c) is significantly different from the SEM image of LiBBM-700 shown in Figure 3a. The EDX analysis of this LiNMC sample in Figure 3d shows Ni, Mn, Co, and O as major elements present, as expected, while we noted that Li is not observed since EDX is not normally sensitive to Li. However, in comparison to the EDX analysis LiBBM-700 shown in Figure 3b, this

EDX plot 3d of regenerated LiNMC shows a negligibly small carbon peak around 0.28 keV, confirming the removal of graphite carbon.

The powder X-ray diffractogram regenerated LiNMC is shown in Figure 4b. In comparison to the LiBBM-700 diffractogram shown above in Figure 4a, the graphite carbon peaks at $2\theta = 26.6^\circ$ and 44.6° are missing in regenerated LiNMC through the removal of graphite. The XRD pattern clearly shows the characteristic peaks of a layered structure for LiNMC described in the literature. The noteworthy peaks at $2\theta = 18.2^\circ$, 22.4° , 33.8° , 37.5° , and 45.2° could be assigned to LiMO₂-type metal oxides where M = Ni, Co, or Mn [36–38]. Most significantly, these peak positions in regenerated LiNMC (Figure 4b) are comparable to X-ray peaks found in the original LiBBM-700 in Figure 4a, confirming the regeneration of similar layered LiNMC structure in mixed hydroxy acid leaching–gel formation–pyrolysis process.

4. Conclusions

We have shown that Li, Ni, Mn, and Co metals can be leached out as their chelated complex from pyrolyzed, combined anode and cathode electrode coating black mass from a DELL 1525 laptop spent Li-ion battery using an aqueous solution mixture of glycolic and lactic acids at 120 °C, in excellent yields, without using hydrogen peroxide or any other reagent. The highest leaching efficiencies of 100, 100, 100, and 89% (*w/w*)% for leaching Li, Ni, Mn, and Co at 120 °C for 6 h. was possible with the use of an aqueous acid mixture of 0.15 M in glycolic and 0.35 M in lactic acids. Evaporation of water from the leaching solution resulted in the formation of mixed metal—hydroxy carboxylic acid chelate sol-gel. Then, drying the sol-gel and pyrolysis at 800 °C in air could be used to regenerate lithium nickel manganese cobalt oxide with an empirical formula $\text{LiNi}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.30}$, which is comparable to the lithium nickel manganese cobalt oxide in the pyrolyzed, combined cathode and anode black material used, $\text{LiNi}_{0.03}\text{Mn}_{0.02}\text{Co}_{0.11}\text{O}_{0.35}$. In conclusion, we have presented a new green leaching method based on a mixture of inexpensive, readily available α -hydroxy carboxylic acids for recovery of Li, Ni, Mn, and Co found in spent Li-ion battery waste electrode material without the use of hydrogen peroxide or other oxidants or reagents. Furthermore, lithium nickel manganese cobalt oxide could be easily regenerated from this leachate solution to a product with a formula comparable to the composition of metals in combined electrode coating without the addition of metal salts or precipitating agents to the leachate solution.

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