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Article

Lithium and Cobalt Recovery from $LiCoO_2$ Using Oxalate Chemistry: Scale-Up and Techno-Economic Analysis

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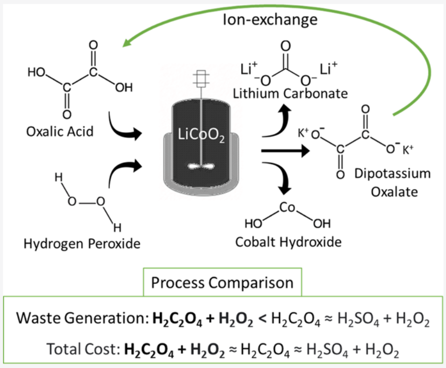
ABSTRACT: Currently, approximately 59% of spent lithium-ion batteries (LIBs) contain a lithium cobalt oxide ($LiCoO_2$) cathode. Both lithium (Li) and cobalt (Co) are critical metals, and the efficient recycling of $LiCoO_2$ cathodes through an environmentally benign process is essential for a stable Li and Co economy. In this work, a closed-loop recycling process utilizing oxalic acid ($H_2C_2O_4$) and hydrogen peroxide (H_2O_2) was scaled-up to operate at a solid-to-liquid (S/L) ratio of 38 g/L. The $H_2C_2O_4$ process was operated at 100 °C with Li_2CO_3 and $Co(OH)_2$ as the final products, whereas in the presence of H_2O_2, the metal extraction was operated at 75 °C. After the metal recovery, the $H_2C_2O_4$ was efficiently recycled using an ion exchange process. A techno-economic analysis was performed to compare the oxalate process with the H_2SO_4 process operating at 65 °C and S/L = 100 g/L. The $H_2C_2O_4$ and $H_2C_2O_4$ + H_2O_2 processes with 90% recycling of oxalate are equal in cost with the H_2SO_4 process on a per kilogram $LiCoO_2$ production basis. An important difference is that the $H_2C_2O_4$ + H_2O_2 process produces 50% less waste than the H_2SO_4 + H_2O_2 process. The $H_2C_2O_4$ and $H_2C_2O_4$ + H_2O_2 processes provide the opportunity to recycle oxalate in order to create a closed-loop, economical, and environmentally friendly process for recovering critical metals such as Li and Co from $LiCoO_2$. The oxalate process offers similar advantages for recycling other valuable metals from ore processing and waste streams.



Waste Generation: $\mathbf{H_2C_2O_4 + H_2O_2}$ < $H_2C_2O_4 \approx H_2SO_4 + H_2O_2$

Total Cost: $\mathbf{H_2C_2O_4 + H_2O_2}$ ≈ $H_2C_2O_4 \approx H_2SO_4 + H_2O_2$

1. INTRODUCTION

Lithium-ion batteries (LIBs) are rechargeable energy storage devices with significant importance in portable electronic goods and electric vehicles. The global LIB market is expected to grow from \$41.1 billion in 2021 to \$116.6 billion by 2030 at a compound annual growth rate (CAGR) of 12.3%.[1] The growing demand for LIBs needs to be coupled with comprehensive recycling to mitigate the scarcity of materials and enhance environmental sustainability. Lithium (Li) and Cobalt (Co) are the two critical metals used in the production of LIBs. For 1 ton of battery-grade Li production, 750 tons of brine or 250 tons of ore is required, whereas 28 tons of spent LIBs contain equivalent mass. Similarly, to produce 1 ton of Co, 300 tons of ore is needed, whereas 5 to 15 tons of spent LIBs can produce an equivalent mass of Co.[2] In 2019, 29,000 tons of spent LIBs were available for recycling in the United States, out of which 59% were lithium cobalt oxide (LCO). The remaining 41% was comprised of lithium nickel−manganese−cobalt oxide (NMC), lithium manganese oxide (LMO), and lithium iron phosphate (LFP).[3]

The LIB recycling technologies can be divided into three main categories: pyrometallurgy, hydrometallurgy, and direct recycling.[4,5] Pyrometallurgy is the most flexible technology and can be adapted for all kinds of LIBs with minimum pre-processing. The thermal treatment of spent LIB waste with reductants such as graphite, aluminum, and ammonium chloride converts transition metal elements into their metal oxides, and Li is converted into lithium salts. In this thermal process, the Li can be selectively recovered by water leaching with high efficiency.[6−8] However, the high energy requirements and significant carbon footprint from fossil-based fuels in pyrometallurgical processes are the major issues.[9] Direct recycling requires physical separation methods to separate the LIB components and efficiently reuse the cathode after re-lithiation. However, the continuously changing cathode chemistries and battery designs are the major obstacles for this technology in the circular battery economy.[10] For the recycling of the predominant LCO batteries, re-lithiation via direct recycling may not be appropriate as the cathode composition cannot be directed toward reducing the dependence on Co. Hydrometallurgy is based on wet chemistry with high efficiency in recovering pure metal compounds. These metal compounds can be used to synthesize new cathode materials. However, pre-processing and separation of individual components from spent LIBs is necessary for effective metal extraction.[5,11] Hydrometallurgical processes are adapt-

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able with the continuously evolving cathode metal oxide formulations and can recycle the LCO batteries into NMC batteries. This technique typically uses strong inorganic acids like sulfuric, nitric, and hydrochloric acid with a reducing agent like hydrogen peroxide.[12] Hydrometallurgical processes using inorganic acids are cost-efficient, but extensive chemical consumption and waste generation, along with significant environmental impacts from SO_x and NO_x emissions, are the major drawbacks.[13,14]

Hydrometallurgical processes using organic acids like oxalic, citric, ascorbic, and succinic acid have also been demonstrated at a lab-scale to recover critical metals from spent LIBs.[15−21] These acids have minimal environmental impacts but are expensive compared to inorganic acids. H_2O_2 is commonly used as a reducing agent along with acids to convert Co^{3+} into the stable Co^{2+} form. Oxalic acid ($H_2C_2O_4$) is unique in its reducing and solubility properties and was identified as a sustainable, green, and environmentally friendly reagent in our previous works.[22] For the hydrometallurgical treatment of $LiCoO_2$ using $H_2C_2O_4$, Li leaches into the solution, whereas Co precipitates out in the form of $CoC_2O_4{\cdot}2H_2O$. This direct separation allows a one-step separation between Li and Co in the recycling process.[22,23] Sun and Qiu recovered 96% of Li from $LiCoO_2$ (solid-to-liquid ratio = 50 g/L) using 1 M $H_2C_2O_4$ at 80 °C in 2 h.[23] Sohn et al. performed the metal extraction from $LiCoO_2$ using 3 M $H_2C_2O_4$ under similar conditions as Sun and Qiu and was able to leach 99% of Li in 1.5 h.[24] Aaltonen et al. used 1 M $H_2C_2O_4$ at 25 °C to extract Li and Co from $LiCoO_2$ at a 5 g/L solid-to-liquid ratio.[16] Only 74% of the Li was leached into the aqueous phase in 24 h.[16] The low leaching efficiency observed by Aaltonen et al. indicates the importance of using high temperatures during the Li and Co extraction from $LiCoO_2$.

In our previous work, $H_2C_2O_4$ was shown to be an efficient reagent to separate and recover Li and Co from $LiCoO_2$.[22] In addition, to offset the cost of expensive $H_2C_2O_4$ and minimize waste generation, a closed-loop process was proposed to regenerate half of the acid after metal precipitations. The $H_2C_2O_4$ regeneration was proposed through a cation exchange process. This work extends and improves our previous work to regenerate and reuse 100% of the $H_2C_2O_4$ through a novel closed-loop process. To the best of our knowledge, no other hydrometallurgical process with oxalic acid has been developed that demonstrates greater than 95% acid recovery and reuse. In addition, the novel precipitation route can achieve Li and Co purities of 99.5%. A techno-economic analysis has been performed comparing our developed closed-loop hydrometallurgical processes of $H_2C_2O_4$ and $H_2C_2O_4$ + H_2O_2 with the H_2SO_4 + H_2O_2 process for recycling LIB cathodes. The flexibility of the oxalate closed-loop process to recycle NMC cathodes and other metallic impurities (from current collector foils and separators) like Fe, Cu, Al, and Zn has also been discussed. This work demonstrates the adaptability and uniqueness of oxalic acid in developing a closed-loop, green, and environmentally friendly recycling process for LiBs.

2. EXPERIMENTAL SECTION

2.1. Materials and Materials Characterization. Lithium cobalt oxide, $LiCoO_2$, (99.8%, Sigma-Aldrich), oxalic acid dihydrate, $H_2C_2O_4{\cdot}2H_2O$, (99.5%, ACROS Organics), lithium nickel-manganese-cobalt oxide, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, (NMC111, MSE Supplies), and hydrogen peroxide, H_2O_2, (30%, Fisher Chemical) were used for the digestion reactions. Potassium carbonate, K_2CO_3, (99%, ACROS Organics) and potassium hydroxide, KOH, (Pellets 85%, Fisher Chemical) were used for the metal precipitations. Amberlyst 15 (Dry H-form, strong acid cation-exchange resin) and sulfuric acid, H_2SO_4, (ACS reagent, Fisher Chemical) were used in the regeneration studies. The stock solution (5 wt %) for ICP-OES was prepared using nitric acid, HNO_3, (ACS reagent, Fisher Chemical). All solutions were prepared in deionized water (18 MΩ cm).

The metal concentration in the aqueous phase was measured using a Varian/Agilent 725 ES inductively coupled plasma−optical emission spectrometer (ICP-OES). Calibration was performed using the standards prepared from the commercial stock solutions. The 5 wt % nitric acid (HNO_3) was used as a diluent for ICP-OES measurements. Solid samples were analyzed on a Bruker D2-phaser powder X-ray diffraction (PXRD) with a Co Kα source (λ = 1.78897 Å), operated at 30 kV and 10 mA.

2.2. Reactor Setup and Sampling. A 1 L glass reactor setup was used for all of the hydrometallurgical experiments in this work.[22] The reactor was enclosed in a heating jacket, and the 5-neck Duran head was connected to an electric agitator, a reflux condenser, and two thermocouples. A 5 mL plastic syringe with a 20 cm long needle was connected to the sampling port (fifth neck of reactor head) to withdraw solid and aqueous samples. The samples were centrifuged for 5 min at 4000 rpm to separate the aqueous and solid phases. The aqueous phase was diluted with 5 wt % HNO_3 at an appropriate ratio to achieve a concentration of less than 10 ppm for every metal in the aqueous phase.

2.3. Experiments: Hydrometallurgy, Precipitation, and Batch Ion-Exchange. All hydrometallurgical experiments were performed in the glass reactor using an aqueous solution of $H_2C_2O_4$ or $H_2C_2O_4$ + H_2O_2. The aqueous solution was heated to a set temperature before adding the cathode material. In this work, the experiments were scaled up to a solid-to-liquid (S/L) ratio of 38 from 15 g/L in our previous work.[22,25] The reactor temperature (T) and agitation speed (N_S) were set at 98 °C and 600 rpm, respectively. The molar ratio between $LiCoO_2$ and $C_2O_4^{2-}$ (Co:OA) is critical and was kept constant at Co:OA = 1:3 (1.16 M $H_2C_2O_4$). In the presence of H_2O_2, the molar ratio between $LiCoO_2$, $C_2O_4^{2-}$, and H_2O_2 (Co:OA:H_2O_2) was maintained at Co:OA:H_2O_2 = 1:1.5:3. This corresponds to a concentration of 0.58 M $H_2C_2O_4$ and 1.16 M H_2O_2 to maintain an S/L ratio of 38 g/L. Both concentrations were optimized in our previous work.[22,25] The S/L ratio of 38 g/L was set to avoid crystallization of $H_2C_2O_4$ in the leachate after cooling to 20 °C.

The pH of the solution was critical to precipitate metal hydroxides and carbonates from an aqueous solution. KOH pellets (85%) were used to regulate the pH of the solution. During the extraction of Li and Co from $LiCoO_2$ using $H_2C_2O_4$, Li remained in the aqueous phase and Co precipitated as $CoC_2O_4{\cdot}2H_2O$. The Li concentration in the aqueous phase after a 38 g/L metal extraction experiment was 2.70 g/L. Lithium carbonate (Li_2CO_3) has an aqueous solubility of 13.3 g/L, which corresponds to the Li concentration of 2.50 g/L; therefore, it is essential to concentrate Li before precipitation. In this work, the aqueous phase was concentrated four times to achieve a Li concentration greater than 10 g/L. This was achieved by evaporating the water to reduce the 1 L of aqueous filtrate to 250 mL volume or reusing the same filtrate to perform three additional metal extraction experiments at the S/L ratio of 38 g/L. Once a Li concentration > 10 g/L was achieved, KOH was added to raise the pH > 13, and the Li was precipitated using K_2CO_3. After the removal of Li, $CoC_2O_4{\cdot}2H_2O$ was added slowly (1 g batches) and KOH was used to maintain the pH > 13 to ensure the precipitation of Co in the form of $Co(OH)_2$.

After precipitating Li and Co, the aqueous solution contained only K^+ as the major cation. In this work, Amberlyst 15 (Dry, H-form), a strong acid cation exchange (SAC) resin, was used to regenerate and recycle $H_2C_2O_4$. Initially, the resins were soaked in 1.5 M H_2SO_4 for 2 h to activate the ion-exchange sites with H^+. The activated resins were washed with DI water until the effluent was a neutral pH (pH ≈ 7). After washing, the activated resins were mixed with the aqueous filtrate for 1−2 h. The aqueous phase predominantly contained K^+, and the $C_2O_4{}^{2-}$ was initially added during the $H_2C_2O_4$ acid addition. The H^+ from the activated resins replaced the K^+ in the solution, and $H_2C_2O_4$ was the predominant oxalate species at a pH ≈ 1. The ion-exchange efficiency was calculated by measuring the concentration of the remaining K^+ ions in the aqueous phase and subtracting it from the initial K^+ concentration. The K-saturated resins were regenerated to the original H-form using 1.5 M H_2SO_4.

3. RESULTS AND DISCUSSION

In our previous work, the reaction conditions for extraction and separation of Li and Co from $LiCoO_2$ were optimized and the mechanism was discussed in detail.[22,25] The critical findings presented in this work are the precipitation of Li and Co, the recycling of $H_2C_2O_4$, and the demonstration of the scaled-up closed-loop process with a techno-economic analysis.

3.1. Li and Co Precipitation Using Potassium Compounds.

Precipitation of metals effectively in the hydroxide or carbonate form requires the stoichiometric addition of precipitation agents in a suitable pH range. Sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were the commonly used precipitation agents for precipitating lithium carbonate (Li_2CO_3) and cobalt hydroxide ($Co(OH)_2$), respectively.[26,27] However, K_2CO_3 and KOH were chosen as the precipitation agents to recover Li and Co in this work based on the solubility advantages. In an oxalate-based system, the high aqueous solubility of by-products was required for efficient metal precipitation. The higher aqueous solubility of $K_2C_2O_4$ (364 g/L)[28] than $Na_2C_2O_4$ (36.1 g/L)[28] at 20 °C (10 times higher) allows the Li_2CO_3 and $Co(OH)_2$ to precipitate efficiently using K_2CO_3 and KOH.

To synthesize LIB cathodes, Li_2CO_3 or LiOH are the preferred Li compounds. Li_2CO_3 has an aqueous solubility of 13.3 g/L (20 °C), whereas LiOH is more soluble with an aqueous solubility of 110 g/L at 20 °C (9 times higher).[28] Hence, Li_2CO_3 was chosen as the Li end product. The precipitation reaction is shown in eq 1. For the precipitation of any carbonate compound, it is necessary to ensure that the CO_3^{2-} ions are the predominant carbonate species in the aqueous phase. Carbonic acid in the aqueous phase has pKa_1 = 6.36 and pKa_2 = 10.33;[29] therefore, at pH = 12.5, 99.5 mol % of the carbonate ions were in the form of CO_3^{2-}.[30] Hence, the pH of the aqueous solution was maintained above 12.5 using KOH during the Li_2CO_3 precipitation. The precipitation of Li in the form of Li_2CO_3 is an endothermic process, resulting in decreased solubility at elevated temperatures;[28,31] therefore, Li precipitation was performed at a temperature of 80 °C to minimize the water loss and achieve the highest efficiency.

$$Li_2C_2O_4(aq) + K_2CO_3(s) \rightleftharpoons Li_2CO_3(s) + K_2C_2O_4(aq) \quad (1)$$

Cobalt was directly precipitated in the form of $CoC_2O_4{\cdot}2H_2O$ during the hydrometallurgical step.[22] The redissolution of $CoC_2O_4{\cdot}2H_2O$ in the minimum number of steps was critical for recovering the $C_2O_4^{2-}$ ions and regenerating the $H_2C_2O_4$. Most of the transition metal oxalates can form soluble metal oxalate complexes in the presence of excess $C_2O_4^{2-}$ ions.[30,32] This property was utilized to dissolve $CoC_2O_4{\cdot}2H_2O$ at a pH above 6. The pKa_2 of $H_2C_2O_4$ is 4.19, and for pH > 6, $C_2O_4^{2-}$ ions become the predominant oxalate species;[30] however, in this basic pH range, dissolved Co^{2+} ions can be precipitated in the form of $Co(OH)_2$.[33] The simultaneous dissolution and precipitation can be employed together to precipitate Co in the form of $Co(OH)_2$ and recover $C_2O_4^{2-}$ ions at pH = 13. These reactions are summarized in eqs 2 and 3.

$$CoC_2O_4{\cdot}2H_2O(s) + K_2C_2O_4(aq) \rightleftharpoons K_2[Co(C_2O_4)_2](aq) \quad (2)$$

$$K_2[Co(C_2O_4)_2](aq) + 2KOH(s) \rightleftharpoons Co(OH)_2(s) + 2K_2C_2O_4(aq) \quad (3)$$

3.2. Ion-Exchange Resins for Recycling of Oxalic Acid.

As discussed in Section 3.1, potassium compounds are preferable for metal precipitation in an oxalate process; therefore, after the Li and Co precipitation, K^+ remains the predominant cation. A strong-acid cation exchange (SAC) resin can be used to exchange the available K^+ with H^+ to regenerate and recycle $H_2C_2O_4$. The SAC resins contain a sulfonic (HSO_3^-) acid group at active sites that can neutralize bases and convert neutral salts into their acidic counterparts.[34,35] The SAC resins can also be regenerated in the presence of excess mineral acids for reuse. In this work, Amberlyst 15 (dry, H-form), a macroreticular polystyrene-based SAC resin, was used to exchange the K^+.

3.2.1. Experimental Capacity and Kinetics of Ion Exchange. For the preliminary understanding of ion exchange, experiments were performed in a batch setup rather than a column setup. The theoretical capacity of Amberlyst 15 was reported as 4.3 meq/g (for dry, Na^+ form).[35] The moisture-holding capacity of the Amberlyst 15 (H^+ form) used in this work was determined to be 55 wt % by drying the wet resins in the air while measuring the weight. To obtain the experimental exchange capacity of resins with K^+, the resins were activated using the method described in Section 2.3. Next, 50 g of wet activated resins were sequentially mixed in 100 mL batches of 1 M KOH solution until saturated. The experimental capacity for Amberlyst 15 was found to be 4.64 meq/g, and the results are presented in Table 1. The capacity of the resins was critical for determining the mass of dry resins required to recycle the acid after metal extraction from $LiCoO_2$. Another important parameter is the contact time required between resins and the aqueous phase in the batch setup operation. Hence, the K concentration in the 100 mL of 1 M KOH solution was tracked after mixing with 50 g of wet resins. The ion exchange (at 20 °C) was completed within the first 15 min of contact, as shown in Figure 1.

3.2.2. Conditions for Regeneration of Resins. Another important study was to determine the conditions for regenerating the K-saturated Amberlyst 15 resins. Approximately 20 g of wet resins (from 50 g wet resin, Table 1) was mixed sequentially with three 40 mL batches of 1.5 M H_2SO_4.

Table 1. Measurement of Exchange Capacity for Amberlyst 15 (Dry, H+ Form)

	K-concentration in the aqueous phase (g/L)		
batch no.	before resin addition	after resin addition	net exchange (meq of K)
1	39.10	2.67	93.18
2	39.10	35.55	9.09
3	39.10	38.21	2.27
4	39.10	38.92	0.45
	total exchange		105 meq of K
	dry weight of resins		22.72 g
	experimental capacity		4.62 meq/g

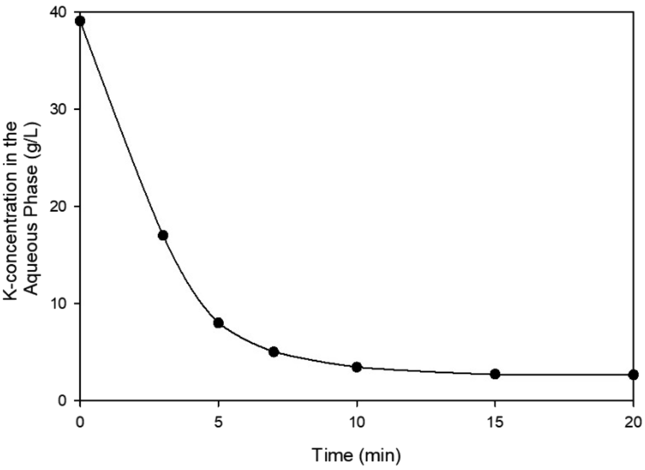

Figure 1. Kinetics of ion exchange with 50 g wet resins in 100 mL of 1 M KOH solution (initial concentration).

The contact time between the resins and 40 mL H_2SO_4 was 30 min. To calculate the regeneration efficiency, the concentration of K in the acidic phase was tracked for every batch, and the results are shown in Table 2. To regenerate 20 g of K-saturated resins into the H-form, at least 120 mL of 1.5 M H_2SO_4 was required. Excess H_2SO_4 was required for the regeneration of SAC resins.[36] In addition, the H_2SO_4 used in the regeneration study shown in Table 2 can be reused for other batches of resin saturated with K^+. To study this hypothesis, 40 mL of 1.5 M H_2SO_4 was mixed with five batches of K-saturated 20 g wet resins. Every resin batch was saturated with approximately 42 meq of K^+. The results shown in Table 3 conclude that the 40 mL of 1.5 M H_2SO_4 resins can partially regenerate each batch of resin saturated with K^+ ions. After contacting five similar batches of K-saturated resins, 39.27 meq of K was extracted. The 39.27 meq of K is 94% of the K present on 20 g saturated resins (1 batch of Table 3). These results were promising, and a process could be designed using recycled and fresh 1.5 M H_2SO_4 for recycling SAC.

Table 2. Regeneration of 20 g Wet Resin Batches Using 1.5 M H_2SO_4

	K-concentration in the H_2SO_4 (g/L)		
batch no.	before resin addition	after resin addition	net exchange (meq of K)
1 (40 mL, 1.5 M H_2SO_4)	0	19.99	20.45
2 (40 mL, 1.5 M H_2SO_4)	0	14.97	15.31
3 (40 mL, 1.5 M H_2SO_4)	0	4.72	4.83
	total exchange		40.59 meq of K
	amount of K on 20 g saturated resins		42 meq
	resin regeneration efficiency		96.6%

Table 3. Extraction of K^+ in a 1.5 M H_2SO_4 Solution (40 mL) from K-Saturated Resin Batches

	K-concentration in the H_2SO_4 (g/L)		
batch no.	before resin addition	after resin addition	net exchange (meq of K)
1 (20 g, K-Resins)	0	17.26	17.65
2 (20 g, K-Resins)	17.26	28.16	11.15
3 (20 g, K-Resins)	28.16	32.95	4.91
4 (20 g, K-Resins)	32.95	36.32	3.44
5 (20 g, K-Resins)	36.32	38.39	2.11
		total exchange	39.27 meq of K

3.3. Demonstration of the Closed-Loop Process Using $H_2C_2O_4$. Based on the dissolution and precipitation of Co in the form of $Co(OH)_2$, a new closed-loop process shown in Figure 2 was designed for Li and Co extraction and separation from $LiCoO_2$ using $H_2C_2O_4$. As discussed in Section 2.3, the hydrometallurgical experiments were performed at a $LiCoO_2$ to $H_2C_2O_4$ molar ratio of 1:3 (1.16 M $H_2C_2O_4$), S/L ratio of 38 g/L, T = 100 °C, and N_s = 600 rpm. The Li and Co extraction kinetics from this experiment are shown in Figure 3 (Li and Co: Fresh Acid). It is important to note that the Co precipitated in the form of $CoC_2O_4{\cdot}2H_2O$ and was not present in the aqueous phase. The balanced chemical reaction between $LiCoO_2$ and $H_2C_2O_4$ is shown in eq 4. In Figure 3, efficient Li extraction kinetics were observed within 1 h and the $LiCoO_2$ corresponding to an S/L ratio of 38 g/L was digested with Li and Co separated in the aqueous and solid phases, respectively.

$$\begin{aligned}&4H_2C_2O_4(aq) + 2LiCoO_2(s)\\&\leftrightarrows Li_2C_2O_4(aq) + 2CoC_2O_4{\cdot}2H_2O(s) + 2CO_2(aq)\end{aligned}\tag{4}$$

The next step after Li and Co separation was to precipitate Li in the form of Li_2CO_3 as shown in Figure 2. The Li concentration in the aqueous phase after the first extraction experiment was 2.65 g/L. The solubility of Li_2CO_3 is 13.3 g/L at 20 °C, and that corresponds to a Li concentration of 2.50 g/L.[28] The difference between the Li concentration in the aqueous phase and soluble Li in the Li_2CO_3 was minimal, and efficient precipitation could not be performed. The aqueous phase can be concentrated by reusing the solution for another extraction experiment. Additional $H_2C_2O_4$ will be required to supplement the $C_2O_4^{2-}$ ions precipitated with $CoC_2O_4{\cdot}2H_2O$. In the lab-scale study performed for this work, the aqueous phase was concentrated by evaporating the water from the aqueous filtrate at 105 °C until the volume was reduced by four times. However, concentrating the solution via evaporation is an energy-intensive process and would not be recommended at the commercial-scale. After concentrating the aqueous phase, Li was efficiently precipitated at 80 °C using KOH and K_2CO_3 at a pH = 13.5. The Li concentration in the aqueous phase decreased from 10.5 to 1.3 g/L resulting in an 87% Li recovery in the form of Li_2CO_3. The precipitate was confirmed as Li_2CO_3 using PXRD, as shown in Figure S1. The

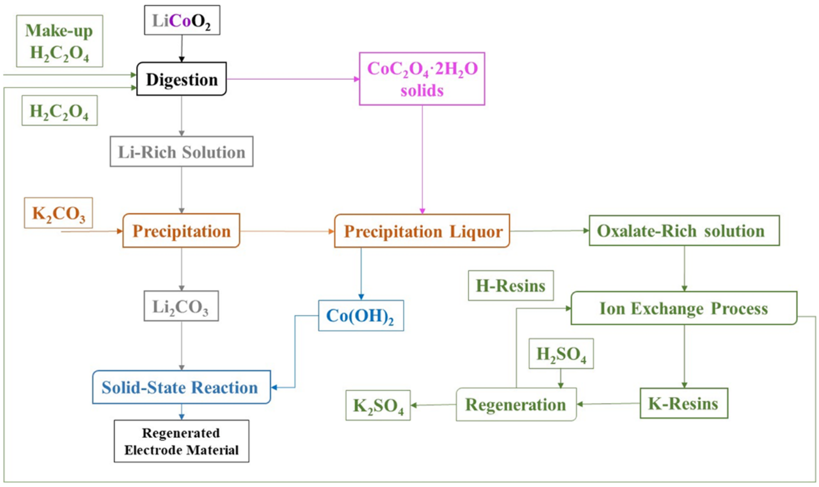

Figure 2. Flowsheet for the proposed closed-loop $LiCoO_2$ recycling process using $H_2C_2O_4$.

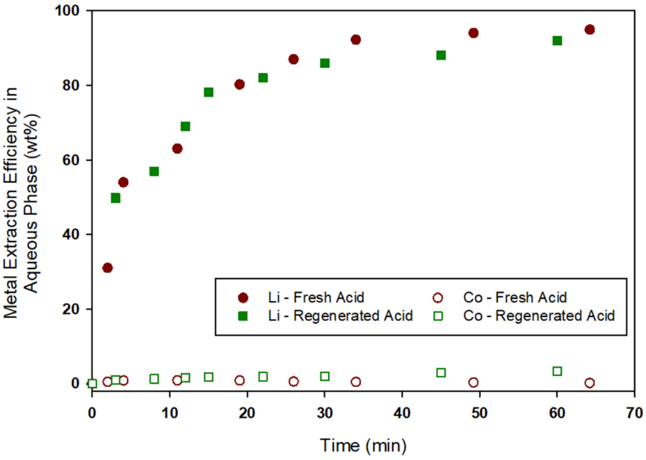

Figure 3. Metal concentration for Li and Co as a function of time in the aqueous phase for fresh and regenerated $H_2C_2O_4$ at Co:OA ratio = 1:3, T = 98 °C, S/L = 38 g/L, and N_S = 600 rpm.

Li_2CO_3 product purity was confirmed to be 97% using ICP-OES.

The precipitation liquor after separating Li had a high pH (pH > 12), and $CoC_2O_4·2H_2O$ was hydrolyzed and precipitated in the form of $Co(OH)_2$ as discussed in Section 3.1. The solid $CoC_2O_4·2H_2O$ was added in small batches while maintaining the pH using KOH, and a dark pink precipitate was recovered. The precipitate was confirmed as $Co(OH)_2$ using PXRD (Figure S2) with a purity of 99.5% determined by ICP-OES.

The precipitated Li_2CO_3 and $Co(OH)_2$ was used to synthesize cathode material through a solid-state reaction. The cathode synthesis involved mixing the solid reactants well and calcining the mixture. $LiCoO_2$ was synthesized from Li_2CO_3 and $Co(OH)_2$ in a 1:2 stoichiometric ratio at 800 °C (eq 5). Other cathode materials like NMC can also be synthesized by adding a stoichiometrically equivalent amount of metal hydroxides along with Li_2CO_3. The $LiCoO_2$ was confirmed using PXRD, as shown in Figure S3.

$$Li_2CO_3 + 2Co(OH)_2 + \frac{1}{2}O_2 \rightarrow 2LiCoO_2 + CO_2 + 2H_2O \qquad (5)$$

Once Li and Co have been separated and recovered, the Amberlyst 15 resins were used to regenerate the $H_2C_2O_4$. The aqueous solution was predominantly $K_2C_2O_4$ with a total K concentration of around 150 g/L. It should be noted that 1 L of the aqueous phase was concentrated to 250 mL during the Li precipitation, leading to a high K concentration. The $H_2C_2O_4$ was regenerated by mixing 90 g of activated Amberlyst 15 resins (dry weight) in the $K_2C_2O_4$ solution for 1 h. The mixture was occasionally mixed, but continuous stirring was avoided to minimize damaging the resin beads. The quantity of resins used in this experiment was based on the optimization studies described in Section 3.2. After 1 h, the K concentration in the aqueous phase was reduced to 500 mg/L resulting in a 99.99% exchange efficiency. The pH of the aqueous phase also dropped from 13.6 to 0.48 after the ion exchange was completed. A 1.5 M H_2SO_4 solution was used to regenerate the acidic sites in the used resins.

The regenerated acid was diluted to the original volume and 10% of the initial $H_2C_2O_4$ was added to make up for the acid lost during precipitation and acid regeneration. The metal extraction from $LiCoO_2$ was performed using the regenerated acid at similar reaction conditions. The Li and Co extraction kinetics in the aqueous phase are shown in Figure 2 (Regenerated Acid). The Li extraction kinetics in the aqueous phase was similar to the fresh acid experiment, and > 90% of Li was extracted within 1 h and > 97% of the Co precipitated in the form of $CoC_2O_4·2H_2O$. The precipitate was confirmed using PXRD (Figure S4). Using the regenerated acid, the efficient metal extraction from $LiCoO_2$ demonstrated the novel closed-loop process with essentially 100% acid recovery.

3.4. Demonstration of the Closed-Loop Process Using $H_2C_2O_4 + H_2O_2$.

In our previous work, the advantages of a $H_2C_2O_4 + H_2O_2$ process have been discussed in detail.[25] A balanced chemical reaction between $LiCoO_2$ and $H_2C_2O_4 + H_2O_2$ is shown in eq 6. In the presence of H_2O_2, the Li and Co extraction can be performed efficiently in around 1 h for temperatures in the range of 55−75 °C using a molar ratio of 1:1.5:3 between $LiCoO_2$, $C_2O_4^{2-}$ and H_2O_2 and at an S/L ratio of 15 g/L.[25]

$$4H_2C_2O_4(aq) + 2LiCoO_2(s) \leftrightharpoons Li_2C_2O_4(aq) + 2CoC_2O_4·2H_2O(s) + 2CO_2(aq) \qquad (6)$$

In this work, a scaled-up process was developed to extract the metals at a S/L ratio of 38 g/L. Based on the results from Section 3.3, a similar closed-loop process could be designed with $H_2C_2O_4$ + H_2O_2 as the extraction reagent, as shown in Figure S5. In the presence of H_2O_2, metal extraction experiments were performed at 75 °C (rather than 100 °C with only $H_2C_2O_4$), and the extraction kinetics are shown in Figure 4 (fresh reagents). More than 90% Li was extracted into the aqueous phase in around 45 min, and Co extraction in the aqueous phase was also minimal. The PXRD patterns confirming the Co products are provided in Figure S6. The Li and Co precipitations were performed as described in Section 3.3. The optimized $H_2C_2O_4$ + H_2O_2 process required 0.58 M of $H_2C_2O_4$, compared to 1.16 M using only $H_2C_2O_4$, described in Section 3.3. In addition, the amount of SAC resins required for regeneration was also reduced by 50%. This difference has a significant impact on the overall economics of the process and will be discussed in Section 3.5. The regenerated $H_2C_2O_4$ was diluted to the original volume, and 10% make-up acid along with fresh H_2O_2 was added to perform metal extractions under similar conditions. The Li extraction kinetics observed using the regenerated acid and fresh H_2O_2 (shown in Figure 4, regenerated acid) were similar to the Li extraction experiments using fresh reagents. The improved kinetics were attributed to the better reduction properties of H_2O_2 than the $C_2O_4^{2-}$ ion.

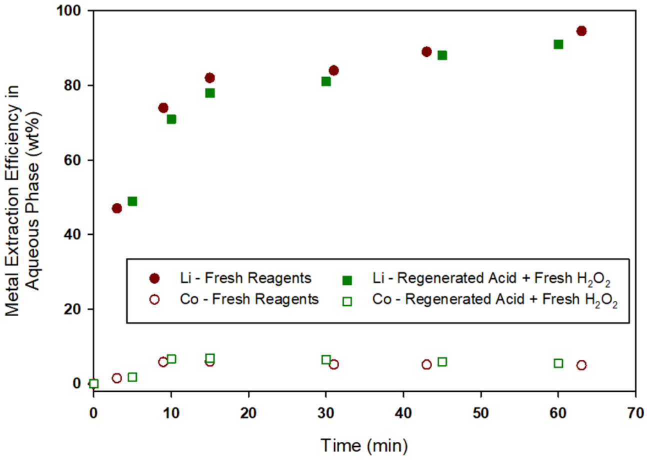

Figure 4. Metal concentration for Li and Co as a function of time in the aqueous phase for fresh and regenerated $H_2C_2O_4$ with H_2O_2 at Co:OA:H_2O_2 ratio = 1:1.5:3, T = 75 °C, S/L = 38 g/L, and N_S = 600 rpm.

3.5. Techno-Economics Analysis. *3.5.1. Comparative Cost Analysis between Different Processes.* To understand the economic impacts of the closed-loop, environmentally friendly oxalate-based process, a preliminary techno-economic model was developed to compare the H_2SO_4 process with two oxalate-based proposed processes. The three different cases used in this study are (A) $LiCoO_2$:$H_2C_2O_4$ in a molar ratio of 1:3 at 100 °C, 1 h, and 38 g/L S/L ratio, (B) $LiCoO_2$:$H_2C_2O_4$:H_2O_2 in a molar ratio of 1:1.5:3 at 75 °C, 1 h, and 38 g/L S/L ratio, and (C) LIB black mass in 2 M H_2SO_4 + 5 vol % H_2O_2 at 60 °C, 2 h, and 100 g/L S/L ratios. Cases A and B are the conditions used in this work for the oxalate process, and the conditions for case C were obtained from Kim et al.[37]

For the energy analysis, the residence time of reaction was considered to be 1 h for cases A and B and 2 h for case C. The feed for cases A and B was $LiCoO_2$, and that for case C was an LIB black mass of NMC cathode. In the work by Kim et al., 100 g of black mass resulted in a total of 0.72 moles of Ni, Mn, and Co metals in the aqueous phase.[37] The 100 g of NMC111 is approximately 1 mole of Ni, Mn, and Co metals stoichiometrically, and it was assumed that the LIB black mass for case C contained 75% of the cathode material. A comparison of these processes is shown in Table 4 based on the cost of reagents for metal extraction ($/kg of cathode material, referred to as $\$/kg_{cm}$ from here on) and the energy cost ($\$/kg_{cm}$). The energy cost included the energy required to achieve and maintain the required temperature for the reaction time. The assumptions used in the energy cost calculations are described in the Supplemental Information (see Section S1). The reagent costs required in the downstream processes for separation of metals were not included in this comparative analysis. Due to variable sources of cathode material, the cost of spent cathode material has also not been included in this analysis. However, the black mass paste cost was reported as $100−200 per metric ton, which contained approximately 50 wt % of carbon, and the rest was spent or unspent metal oxides, along with miscellaneous pieces of plastics and other metals.[38] The bulk prices of chemical reagents were used in this analysis are provided in the Supplemental Information (see Table S1).

Table 4. Cost Comparison between Cases A, B, and C for the First Cycle

	price ($\$/kg_{cm}$)[a]		
	case A: $H_2C_2O_4$	case B: $H_2C_2O_4$ + H_2O_2	case C: H_2SO_4 + H_2O_2
total energy cost	0.12	0.09	0.11
cost of acid	1.9	1.0	0.7
cost of reducing agent	0.0	0.7	0.5
total cost	2.00	1.80	1.30

[a] $\$/kg_{cm}$ = Price in $ for processing 1 kg of cathode material.

The recycling of $H_2C_2O_4$ for metal extraction using the ion-exchange resin process was a novelty of this work. The SAC resins typically have a lifetime of over 10 years; therefore, in the economic comparisons, it was assumed that the resins could be regenerated after each cycle and reused again to recycle $H_2C_2O_4$. In this analysis, 1 kg of cathode material and 100 cycles are assumed for making economic comparisons shown in Table 5. A 90% $H_2C_2O_4$ recycling efficiency was assumed based on experiments with the ion-exchange resins, and an additional 10% $H_2C_2O_4$ make-up was added, as discussed in Sections 3.3 and 3.4. The bulk prices of reagents used in the analysis are shown in Table S1. In Table 4 (1 cycle, no acid recycling), the total cost of the $H_2C_2O_4$ (case A) and $H_2C_2O_4$ + H_2O_2 (case B) are in the similar range ($2/kg and $1.8/kg) but the H_2SO_4 + H_2O_2 (case C, $1.3/kg) process was 30% cheaper. The lower cost is due to the operation of case C at an S/L ratio of 100 g/L by Kim et al.,[37] whereas cases A and B were operated at an S/L ratio of 38 g/L. In the case of recycling 90% of $H_2C_2O_4$, both cases A and B have the reagent cost in a similar range as case C ($\$130/\ 100kg_{cm}$). In addition, the E-factor defined by eq 7 was used to compare all three cases as shown in Table 6.

$$\mathrm{E-factor} = \frac{\text{total waste produced (kg)}}{\text{total product (kg)}} \tag{7}$$

For an ideal process, the E-factor should be zero. In case A and case B, H_2SO_4 acid used for the recycling of $H_2C_2O_4$ was

Table 5. Cost Comparison between Cases A, B, and C over 100 Cycles

	price ($/100 kg_{cm})[a]		
	case A: $H_2C_2O_4$	case B: $H_2C_2O_4$ + H_2O_2	case C: H_2SO_4 + H_2O_2
total energy cost	12	9	12
cost of SAC resins (bulk price = $3/kg)	23	11	0
cost of SAC resins (bulk price = $5/kg)	38	19	0
cost of SAC resins (bulk price = $7/kg)	53	27	0
cost of acid (including make-up)	21	11	65
cost of H_2O_2	0	71	54
cost of H_2SO_4 for regeneration of resins	56	28	0
total cost	127 ± 15	138 ± 9	131

[a] $/100 kg_{cm} = Price in $ for processing 100 kg of cathode material.

Table 6. Comparison of Waste Production and E-Factor between Cases A, B, and C over 100 Cycles

	case A: $H_2C_2O_4$	case B: $H_2C_2O_4$ + H_2O_2	case C: H_2SO_4 + H_2O_2
total waste produced (kg/100 kg_{cm})	1500	750	1300
expected pH of waste	1.5−2.0	1.5−2.0	13−13.5
total product (kg/100 kg_{cm})	132	132	132
E-factor	11.3	5.6	9.8

the major waste stream. This waste acid has a high K concentration and could be used as a fertilizer after appropriate neutralization, which would reduce the E factor even further.[39,40] However, for this analysis, the H_2SO_4 containing K was assumed to be a waste. For case C, the aqueous phase remaining after metal recovery was considered a waste. The pH of this waste stream for case C was assumed to be around 13−13.5 because of the metal hydroxide precipitations performed. Among the cases discussed in this section, case B ($H_2C_2O_4$ + H_2O_2) has the lowest E-factor with comparable economics with the H_2SO_4 + H_2O_2 process. Additional improvements in waste minimization could lower the E factor even further for the oxalate process and should be explored.

3.5.2. Profit Analysis for Oxalate Process. The LIB recycling process was driven by the value associated with the transition metal products, particularly Co. The battery chemistries are continuously evolving to reduce the dependence on Co in the cathode; therefore, the profit associated with any recycling technologies was the most sensitive to the market price of products such as $Co(OH)_2$. The impact of the variable market price of $Co(OH)_2$ was analyzed on the profit margin of both processes ($H_2C_2O_4$ and $H_2C_2O_4$ + H_2O_2) developed in this work. Currently, the market price of $Co(OH)_2$ is around $30/kg (Table S1). For this analysis, this market price was considered the best-case, and $5/kg was considered the worst-case scenario. The worst-case scenario also explains the economic impact of using the oxalate process to recycle an NMC cathode or even a Co-free cathode. The total input cost includes the costs described in Table 5, along with the reagents (K_2CO_3 and KOH) required for metal precipitations. The K_2CO_3 and KOH are the preferred precipitation reagents compared with Na_2CO_3 and NaOH because of the high aqueous solubility of $K_2C_2O_4$ (36.4 g/100 mL at 20 °C) compared to $Na_2C_2O_4$ (3.41 g/100 mL at 20 °C). This was a critical discovery for achieving the high purity products (i.e., 99.5%) of Li and Co. If even higher purity is required for LIB battery applications (i.e., 99.9%), additional purification steps should be considered. It was also found that the net profit is sensitive to the number of cycles the resins can be reused. In order to understand this impact, the number of times the resins could be reused was varied from 10 to 150 (e.g., Table 5, 100 cycles). The variation in the net profit with varying cobalt hydroxide market price (best-case to worst-case) and SAC resins expected life (number of recycling cycles) for the $H_2C_2O_4$ + H_2O_2 process are shown in Figure 5. In the case of $H_2C_2O_4$ as the extraction reagent, the net profit was approximately 5% lesser in every case. For the worst-case scenario, the $H_2C_2O_4$ process becomes profitable after 25 cycles and for $H_2C_2O_4$ + H_2O_2, the process is profitable at even 10 cycles. Overall, the $H_2C_2O_4$ + H_2O_2 process was slightly more profitable and had a smaller E-factor than the $H_2C_2O_4$

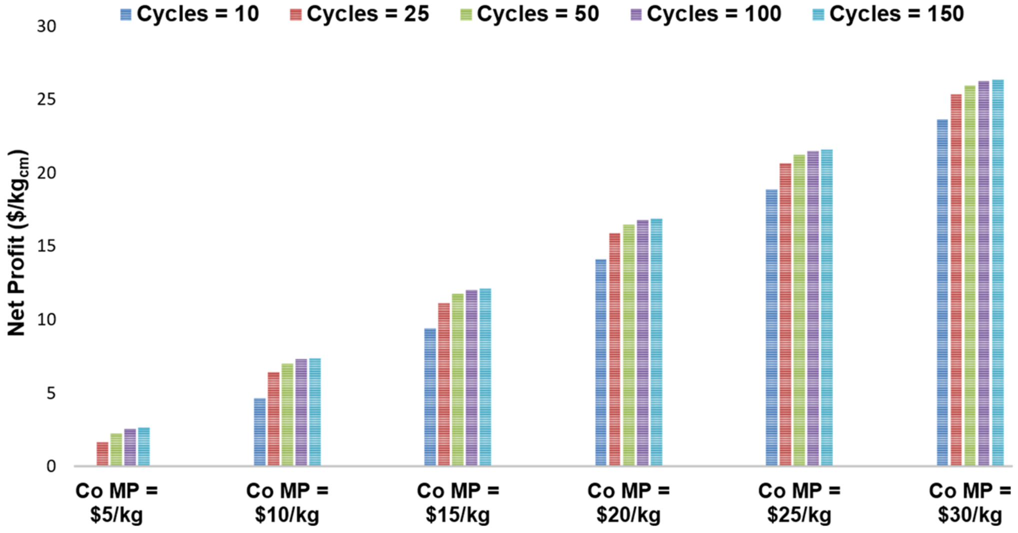

Figure 5. Net profit sensitivity toward the market price of $Co(OH)_2$ and number of cycles for the metal extraction using $H_2C_2O_4$ + H_2O_2. Co MP corresponds to the market price of $Co(OH)_2$.

process. Without no recycling of the oxalic acid (i.e., number of cycles = 0), the $H_2C_2O_4$ and $H_2C_2O_4 + H_2O_2$ processes are not profitable due to the initial cost of the acid. However, with acid recycling, both processes ($H_2C_2O_4$ and $H_2C_2O_4 + H_2O_2$) are profitable even using the worst-case scenario for cobalt hydroxide market price (e.g., 20% of market price). An important conclusion is that the cost to recover these critical metals and recycle the acid is less expensive that mining virgin sources of Li and Co. The $H_2SO_4 + H_2O_2$ process discussed in the previous section was not compared because of the variability in the metal separation strategies. In the $H_2SO_4 + H_2O_2$ process, Li and Co will be leached into the aqueous phase and recovery of Co from the mixture will be an expensive process. In the oxalate-based processes, Co and Li are separated into different phases and a one-step separation was possible.

3.6. Flexibility of the Closed-Loop Oxalate Chemistry Process for Other Metal Recovery. The cathode chemistry in LIB production is constantly evolving to reduce Co and replace with other metals such as Ni and Mn. Furthermore, other low-cost metals such as Al, Cu, and Zn along with graphite might be present in the LIB waste. To showcase the flexibility of the oxalate process for separating additional metals, an alternative process shown in Figure 6 was proposed.

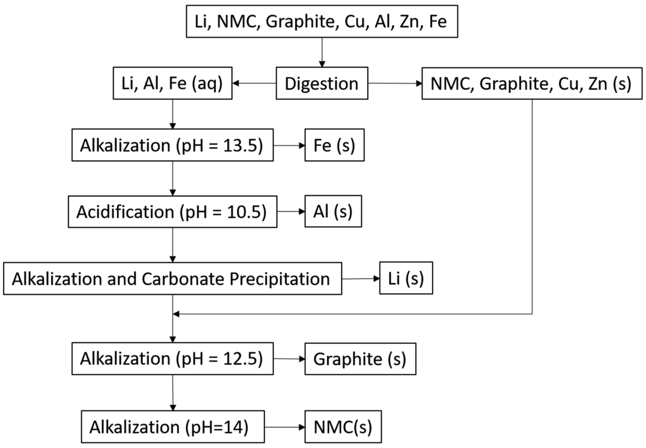

Figure 6. Proposed process for expanding the oxalate process to recycle LIB cathodes with various metal impurities.

To prove that the cathode chemistries involving Ni, Mn, and Co can be recycled conveniently using $H_2C_2O_4$, metal extraction experiments were performed on a $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) material. The NMC cathode has a similar structure to $LiCoO_2$, and using similar metal extraction conditions ($T = 100$ °C, NMC:OA:H_2O_2 = 1:1.5:3, $N_S = 600$ rpm and S/L ratio = 15 g/L), >90% Li was extracted into the aqueous phase and a mixed insoluble metal oxalate containing Ni, Mn, and Co metals was recovered in the solid phase.

The process utilized the property of amphoteric metal hydroxides such as Al, Cu, and Zn to separate them from the NMC material hydroxides at higher pH. Similar to the processes demonstrated in this work, Li has to be precipitated before the addition of the NMC oxalate. If any Fe^{3+} and Al^{3+} impurities are present, they can be selectively precipitated in the form of the respective metal hydroxides, as demonstrated in our previous work for bauxite ore.[41] The higher solubility of $Li(OH)_2$ compared to Fe and Al hydroxides will retain Li in the aqueous phase for Li_2CO_3 precipitation. In the oxalate-rich basic solution after Li precipitation, the solid product comprising insoluble metal oxalates and graphite can be added slowly. In the presence of excess oxalate ions, insoluble metal oxalates should dissolve, leaving graphite as the residue. The pH can be controlled to precipitate NMC hydroxide from the mixture selectively. This process is based on our understanding of the oxalate and hydrolysis chemistry. The research investigations are ongoing, and the results will appear in future publications.

4. CONCLUSIONS

In summary, oxalate chemistry provided a closed-loop and environmentally friendly LIB recycling process that was economical compared with the incumbent H_2SO_4 process. A closed-loop process was designed for recycling 100% of the $H_2C_2O_4$ used after an efficient metal extraction and precipitation. The optimized conditions for the Li and Co extraction from $LiCoO_2$ were scaled-up to a solid-to-liquid ratio of 38 g/L using $H_2C_2O_4$ and $H_2C_2O_4 + H_2O_2$ reagents. The $H_2C_2O_4$ process can completely extract and separate Li and Co within 1 h at 100 °C, whereas $H_2C_2O_4 + H_2O_2$ can perform a similar extraction at 75 °C. The Li present in the aqueous phase can be efficiently precipitated to Li_2CO_3 using potassium carbonate. The precipitated $CoC_2O_4{\cdot}2H_2O$ was dissolved and reprecipitated in the form of $Co(OH)_2$, and a 100% recovery of $C_2O_4^{2-}$ ions in the aqueous phase was achieved. An ion exchange process was designed using strong acid cation-exchange resins to regenerate the $H_2C_2O_4$ from $C_2O_4^{2-}$ ions in the aqueous phase.

A preliminary techno-economic analysis of the $H_2C_2O_4$ and $H_2C_2O_4 + H_2O_2$ processes was performed to evaluate the economic and environmental impacts. The analysis concluded with 80−90% recycling of $H_2C_2O_4$ in the $H_2C_2O_4$, and $H_2C_2O_4 + H_2O_2$ processes are cost competitive with the H_2SO_4 process. To understand the environmental impact, the waste generation and E-factor was calculated. The $H_2C_2O_4 + H_2O_2$ process has an E-factor of 5.5, whereas $H_2C_2O_4$ and H_2SO_4 processes have an E-factor of approximately 10. The 50% reduction in waste generation with similar economic impacts makes the $H_2C_2O_4 + H_2O_2$ process the most sustainable for recovery of critical metals such as Li and Co from waste LIB cathodes. In addition, other valuable metals in LIBs such as Ni and Mn form insoluble metal oxalate dihydrates. These compounds can be dissolved and precipitated selectively in excess oxalates without impurity metals like Al, Cu, and Zn. The low cost and efficient metal separation combined with 50% lower waste generation relative to the H_2SO_4 process makes the oxalate process quite attractive for recovery of critical metals from LIBs. The closed-loop processes discussed in this work can also be used to sustainably recover critical and precious metals from other sources such as ores like bauxite, ilmenite, spent catalysts, and rare-earth containing materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c04876.

PXRD spectrum of solids recovered during lithium precipitation (Figure S1); PXRD spectrum of solid recovered during cobalt precipitation (Figure S2);

PXRD spectrum of product of reaction between Li_2CO_3 and $CoOH)_2$ (Figure S3); PXRD spectra of the precipitate recovered from $LiCoO_2$ digestion using fresh and regenerated $H_2C_2O_4$ (Figure S4); flowsheet of the closed-loop $LiCoO_2$ recycling process using $H_2C_2O_4$ + H_2O_2 (Figure S5); PXRD spectra of the precipitate recovered from $LiCoO_2$ digestion using fresh and regenerated reagents (Figure S6); and bulk prices of chemical reagents used in the techno-economic analysis (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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