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Extraction of Nickel Cobalt and Manganese from Spent NMC Cathodes by Malonic Acid Leaching

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ABSTRACT

This study investigates the feasibility of using malonic acid as a standalone leaching agent for the extraction of nickel, cobalt, and manganese from NMC-type cathode mass without the addition of external reducing agents. A systematic optimization of the leaching process parameters, including acid concentration, temperature, solid-to-liquid ratio, and contact time, was performed. It was established that the optimal process conditions are a malonic acid concentration of 2 M, a solid-to-liquid ratio of 20 g/L, a temperature of 60 °C, and a contact time of 80-90 min. Under these parameters, extraction rates of 98% for nickel, 97% for manganese, and 93% for cobalt are achieved. Increasing the temperature above 60 °C leads to efficiency decrease due to thermal decarboxylation of malonic acid. The addition of hydrogen peroxide under optimal conditions does not improve but rather decreases extraction efficiency. The high efficiency is attributed to the dual function of malonic acid, acting simultaneously as an agent for acidic breakdown of the oxide lattice and as a chelating ligand stabilizing metal ions in solution.

1. Introduction

The rapid growth of the electric vehicle and portable electronics market inevitably leads to an increase in the volume of spent lithium-ion batteries (LIBs) [1, 2]. According to forecasts by the International Energy Agency, the global electric vehicle fleet could reach 140 million units by 2030, which will result in the generation of millions of tons of waste [3, 4]. Spent LIBs contain toxic components and heavy metals that pose a threat to ecosystems if disposed of improperly [5, 6]. At the same time, cathode materials of the $LiNi_xMn_yCo_zO_2$ (NMC) type are rich in strategically important metals – lithium, cobalt, nickel, and manganese, the content of which significantly exceeds their concentration in natural ores [7]. Thus, recycling LIBs is not only an environmental necessity but also an economically viable method of closing the resource loop.

Existing industrial recycling methods are divided into pyrometallurgy and hydrometallurgy [8]. Pyrometallurgical methods require high energy inputs (>1000 °C) and often lead to the loss of lithium in slags [9, 10]. Traditional hydrometallurgy using inorganic acids (H_2SO_4, HCl, HNO_3) ensures high extraction efficiency but is associated with the emission of toxic gases (Cl_2, SO_3, NO_x), equipment corrosion, and the generation of acidic effluents [11, 12]. In this regard, increasing attention is being paid to leaching with organic acids (citric, malic, oxalic, etc.), which are biodegradable, less corrosive, and capable of acting simultaneously as leaching agents and chelators [13, 14].

Researchers have tested a wide range of organic acids for leaching cathode materials. Li et al. demonstrated the high efficiency of lactic acid, achieving over 97% extraction of target metals at 70 °C; however, a high reagent concentration and precise control of reaction time were required [15]. Zheng et al. and Chen et al. investigated citric acid at an optimal temperature of about 90 °C, which is energy-intensive on an industrial scale [16]. Oxalic acid allows for the effective transfer of lithium into solution, but cobalt and nickel precipitate almost instantly as insoluble oxalates, complicating the technological scheme [17]. Tartaric and succinic

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acids are capable of extracting up to 99% of metals, but only in the presence of a significant amount of hydrogen peroxide [18].

In recent years, malonic acid has attracted increasing attention due to its unique chelating properties. Fan et al. conducted a detailed study of the mechanism of leaching NMC cathodes with malonic acid with the addition of hydrogen peroxide and, using density functional theory calculations, showed that malonic acid forms thermodynamically stable complexes with metals [19]. Sohbatzadeh et al. established that malonic acid possesses stronger coordination properties compared to L-glutamic acid and even exhibits reducing activity, which allows for reducing the need for external reducing agents [20]. Li et al. proposed a synergistic system “sulfuric acid – malonic acid” in which malonic acid acts as a complexing agent preventing metal co-precipitation [21].

However, despite these results, a key practical question remains insufficiently clarified: whether malonic acid can ensure effective leaching of industrial NMC cathode mass independently, without the addition of an external reducing agent. Given its dual functionality – acidic attack on the oxide lattice and stabilization of metal ions in solution through complexation – it is logical to hypothesize that this mechanistic set alone might be sufficient to transfer Ni, Co, and Mn into soluble forms under optimally selected conditions. To test this hypothesis, the present work investigates the leaching of industrial NMC black mass with malonic acid solutions without adding an external reducing agent. Optimization of acid concentration, solid/liquid ratio, temperature, and contact time was performed.

2. Experimental part

Spent lithium-ion batteries of various types recovered from household electronic devices were used as the material under investigation. Before starting the experiments, the batteries were cleaned of external plastic coating and insulation. To ensure safety, they were fully discharged to a voltage of less than 1 V using a resistance box (R = 0.2 Ohm). The discharged batteries were shredded using an SCT-100g laboratory shredder with a loading coefficient of 20-25%. This resulted in a fragmented mixture containing cathode and anode materials, electrolyte residues, separator fragments, and metal foil.

To remove residual organic electrolyte, the shredded mixture was dried in an ES-4610 drying oven at 200 °C for 12 h. The dried mass was subjected to fractional separation on an RP 200 N vibratory sieve. Separation was carried out for 7 min at an oscillation amplitude of 1.5 mm using sieves with mesh sizes of 500, 250, and 100 µm. The fraction <100 µm provided the highest yield. This fraction was selected for further leaching experiments because it predominantly corresponds to the dispersed electrode (active) mass, whereas coarser fractions contain a higher proportion of mechanical impurities – separator fragments and aluminum and copper metal foils.

Leaching experiments were performed in closed glass flasks to minimize evaporation losses. A 1.0 g portion of cathode material was contacted with an appropriate volume of malonic acid solution of the desired concentration to achieve the target solid-to-liquid ratio. When heating was required, the flask was placed on a sand bath under constant stirring. After the preset contact time, the suspension was filtered, the solid residue was washed with distilled water, and the filtrate was quantitatively transferred to a volumetric flask and diluted to 250 mL.

The variable process parameters were: malonic acid concentration (0.5-3.0 M in 0.5 M steps), temperature (25-70 °C), solid/liquid ratio (S/L, 20-100 g/L), contact time (10 min – 24 h), and H_2O_2 concentration (0-8 vol.%). Malonic acid concentrations were chosen to control acidity levels, stringent typical hydrometallurgical leaching regimes of cathode materials (where sulfuric acid is frequently employed in the molar range of ~2 M together with a reductant such as H_2O_2), and to determine what the conditions of its reagent deficiency are, as well as excess, for a system where the organic concentration controls the constant function of the leaching agent and complexing agent [22]. The upper limit (3.0 M) is practically feasible because malonic acid is highly soluble in water at room temperature. The temperature range (25-70 °C) was selected to span from ambient conditions up to the threshold where thermal degradation of malonic acid. The chosen S/L range (20-100 g L^{-1}) covers commonly reported solid loadings in black-mass leaching and captures the practical trade-off between extraction efficiency and process throughput/reagent consumption [23]. The S/L ratio was varied by changing the leachant volume at a constant solid mass (1.0 g): 50 mL for 20 g L^{-1} and 10 mL for 100 g L^{-1}. The contact time of 10 min – 24 h was chosen to describe both the initial dissolution kinetics and the system’s reaching a quasi-equilibrium state.The H_2O_2 concentration (0-8 vol.%) was varied as a separate comparative factor: the lower limit of 0 vol.% corresponds to a system without additives, and extending the upper limit of the range ensures testing the hypothesis about the possible influence of the reducing agent even at higher dosages.

The concentrations of Ni, Co, and Mn in solutions after complete digestion of the initial black mass in aqua regia, as well as in the filtrates after leaching, were determined by atomic absorption spectroscopy using a Shimadzu AA-6200 spectrometer (Japan). The extraction degree was calculated as the ratio of the mass of the metal in the filtrate to its total content in the initial sample. The phase composition of the black mass was analyzed by powder X-ray diffraction on a TD-3700 diffractometer (Tongda, China) equipped with a copper radiation source ($\lambda(\text{Cu K}\alpha_1) = 1.54056$ Å; $\lambda(\text{Cu K}\alpha_2) = 1.54439$ Å).

3. Results and Discussion

Before conducting the leaching experiments, it was necessary to establish the phase and elemental composition of the cathode material recovered from spent lithium-ion batteries. To identify the crystal structure of the active phase, X-ray diffraction (XRD) analysis of the homogenized black mass was performed.

The obtained diffractogram (Fig. 1) shows a set of characteristic reflections corresponding to a layered structure of the α-$NaFeO_2$ type (space group R-3m), which is typical for cathode materials with the composition $LiNi_xMn_yCo_zO_2$ (NMC). The diffraction peaks are indexed to the planes (003), (101), (006)/(012), (104), (015), (107), (018), (110), and (113), confirming the presence of a layered oxide phase. It should be noted that XRD data alone cannot uniquely identify the specific type of NMC phase or the exact Ni:Co:Mn ratio, as significant overlap of diffraction reflections is observed in the $LiNi_xMn_yCo_zO_2$ system due to the similarity of crystal lattice parameters and the continuous nature of the solid solutions. Therefore, additional analytical methods were required to refine the elemental composition.

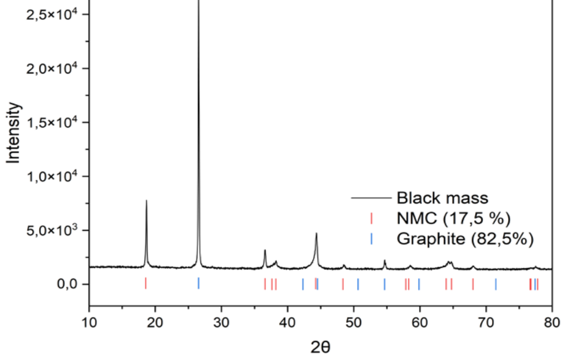

Fig. 1. X-ray diffractogram of the black mass from spent lithium-ion battery cathode material.

To determine the actual metal content in the cathode material, the sample was completely dissolved in aqua regia followed by analysis using atomic absorption spectroscopy (AAS). According to the obtained data, the metal content in the initial cathode mass was: Ni – 230.44 mg/g (23.04 wt.%), Mn – 3.34 mg/g (0.33 wt.%), and Co – 30.73 mg/g (3.07 wt.%). These values were subsequently used as a baseline for calculating metal extraction efficiency in the experiments with malonic acid.

In the subsequent part of the work, the efficiency of malonic acid as a standalone leaching agent for industrial spent NMC cathode mass without the addition of an external reducing agent was investigated. This approach stems from the desire to minimize the use of aggressive reagents and simplify the technological scheme for black mass recycling. Malonic acid is of interest because it combines two key functions for leaching: it provides acidic attack on the oxide lattice through protonation of oxygen sites and weakening of M–O bonds, and acts as a chelating ligand, stabilizing $Ni^{2+}/Co^{2+}/Mn^{2+}$ in solution. Based on this dual role, we hypothesized that malonic acid could ensure effective extraction of target metals from real industrial NMC raw materials without the use of external reducing agents.

To test this hypothesis, leaching was carried out in 2 M $C_3H_4O_4$ at 25 °C, varying the contact time. The kinetic curves (Fig. 2a) demonstrate an increase in the extraction of Ni, Mn, and Co during the first 150-160 min, followed by a plateau. Under these conditions, a pronounced process selectivity is observed: nickel is extracted most efficiently, reaching 42% in 160 min, while manganese extraction is 33.8%, and cobalt extraction is 27.2%. The differences in leaching rate and extent may be attributed to the varying stability of M–O bonds in the layered NMC oxide structure, as well as the specific complexation characteristics of the respective ions with the malonate anion. The results confirmed the fundamental viability of the system and allowed for a systematic optimization of the process parameters.

To determine the optimal concentration of the leaching agent, the effect of malonic acid content was studied in the range of 0.5-3.0 M at a fixed contact time of 150 min and a temperature of 25 °C (Fig. 2b). The dependence of extraction efficiency on acid concentration exhibits an extremum with a maximum at 2 M for all three metals: at this concentration, extraction reaches 42% for Ni, 33% for Mn, and 25% for Co. A further increase in malonic

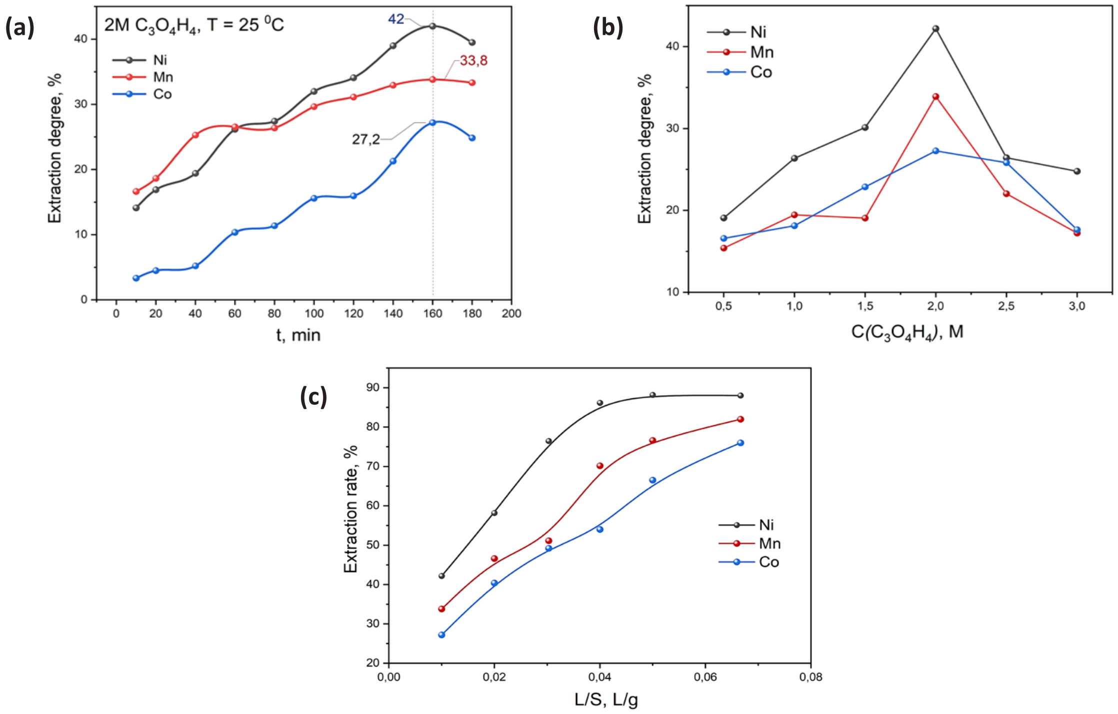

Fig. 2. Effect of leaching parameters on the extraction of Ni, Mn, and Co from NMC cathode mass: (a) leaching profiles at 25 °C and 2 M malonic acid concentration; (b) dependence on malonic acid concentration; (c) dependence on the liquid-to-solid ratio (L/S).

acid concentration leads to a decrease in process efficiency. This is likely due to the shift of equilibria towards the formation of less soluble metal forms in the presence of excess malonate anions, specifically the potential precipitation of malonates and/or the formation of neutral complexes, as well as changes in acid-base equilibrium and an increase in the ionic strength of the solution.

To establish the optimal solid-to-liquid ratio, the effect of cathode material loading (S/L) was investigated in the range of 15-100 g/L at the optimal malonic acid concentration of 2 M (Fig. 2c). Decreasing the solid loading (i.e., increasing the liquid-to-solid ratio, L/S) predictably improves the extraction of all target metals. For nickel, which constitutes the predominant fraction in the NMC-811 cathode composition, the extraction curve approaches a plateau at L/S = 0.05 L/g (S/L = 20 g/L), reaching 88%. At this ratio, extraction efficiencies for manganese and cobalt are 77% and 67%, respectively. Given that nickel represents the major metallic component of the cathode material, and considering the observed plateau behavior indicating near-complete nickel extraction, an S/L ratio of 20 g/L was selected as optimal for subsequent experiments. Further reduction of solid loading (L/S = 0.066 L/g, or S/L ≈ 15 g/L) yields only marginal improvements, which do not justify the proportionally higher consumption of leaching agent and increased solution volumes in industrial implementation.

To determine the temperature dependence of the process, leaching was conducted in the range from 25 to 70 °C at the established optimal parameters: 2 M acid concentration, 20 g/L loading, and 150 min contact time (Fig. 3a). Increasing the temperature from 25 to 60 °C is accompanied by a substantial increase in the extraction of all metals; at 60 °C, maximum values of 98% for Ni, 99% for Mn, and 93% for Co are reached, indicating the intensification of the acidic breakdown of the oxide phase and acceleration of mass transfer under moderate heating. However, a further temperature increase to 70 °C leads to a sharp decrease in extraction, most pronounced for Co and Ni. One possible explanation for this effect is a decrease in the “effective” concentration of the active leaching/complexing agent due to thermal degradation of malonic acid. At pH 2.27 (2 M solution), malonic acid is present almost entirely in the undissociated form H_2Mal (α_0 ≈ 99.7%), which can undergo decarboxylation and is described by first-order kinetics [24]. Estimation using x=1-exp(-kτ) and the Arrhenius equation:

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right)$$

with E_a = 120 kJ·mol^{-1} and A = 1.31×10^{13} s^{-1} [25] gives k ≈ 2.00×10^{-6} s^{-1} at 60 °C and k ≈ 7.06×10^{-6} s^{-1} at

70 °C. Over 150 min, this corresponds to decomposition of approximately ~1.78% and ~6.15%, respectively. These values indicate faster degradation at 70 °C. However, their magnitude is too small to explain the sharp drop in extraction observed in the experimental curve within a homogeneous bulk-solution decomposition model. At the same time, in the real heterogeneous "solution-solid" system, malonic acid losses may exceed those predicted for the neat solution, since the NMC surface may potentially catalyze its decomposition. Therefore, 60 °C is the most rational temperature, providing high leaching kinetics while maintaining acceptable thermal stability of the reagent.

To study the process kinetics in detail at the optimal temperature, the time dependence of metal extraction was obtained at 60 °C (Fig. 3b). The process is characterized by a high initial extraction rate: within the first 20 min, nickel extraction reaches 40%, manganese 30%, and cobalt 22%. Maximum extraction values are achieved in the interval of 80-90 min, amounting to 98% for nickel, 96.8% for manganese, and 93.3% for cobalt. With a further increase in contact time, a slight decrease in the extraction of all metals is observed, which may be due to the partial re-precipitation of dissolved species in the form of secondary phases or the continued degradation of the leaching agent.

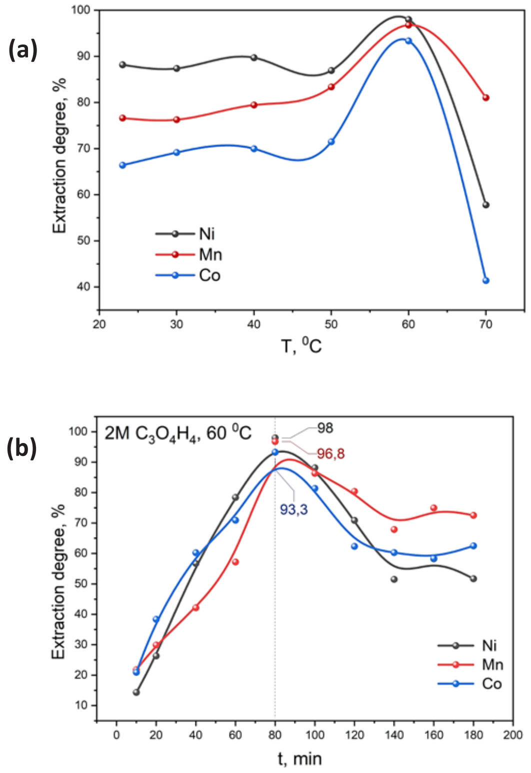

Fig. 3. Effect of temperature on the leaching process: (a) dependence of Ni, Mn, and Co extraction on temperature at a fixed contact time of 150 min; (b) leaching profiles at the optimal temperature of 60 °C (2 M malonic acid, 20 g/L).

To evaluate the feasibility of introducing an additional reducing agent, a comparative study of leaching in the presence of hydrogen peroxide was conducted. In the literature, H_2O_2 is traditionally considered an effective reductant for converting Co^{3+} and Mn^{4+} into more soluble divalent forms, and several studies demonstrate the positive effect of its addition in systems with malonic acid. Fig. 4 presents the dependence of metal extraction on hydrogen peroxide concentration under the established optimal leaching conditions (2 M malonic acid, 20 g/L, 60 °C, 90 min). In our experiments, the addition of H_2O_2 did not lead to improved performance but, on the contrary, caused a noticeable decline. Already at a peroxide concentration of 1 vol.%, cobalt extraction decreased from 93% to 66%; at 8 vol.% H_2O_2, nickel extraction dropped to 56% and cobalt to 44%, while manganese showed the least sensitivity with a drop to 73%.

This result, at first glance, contradicts literature data; however, it should be considered that hydrogen peroxide is a thermally unstable reagent whose effectiveness depends significantly on the combination of temperature, contact time, acid concentration, and solid/liquid ratio. In a number of published works, the optimal conditions for using the malonic acid–H_2O_2 system involve lower acid concentrations, shorter contact times, and different temperature regimes (regimes (e.g., 1.5 M malonic acid, 80 °C, 30 min, S/L = 30 g·L^{-1}, with ~0.5 vol.% H_2O_2 [19]), highlighting the need for careful, joint optimization of all parameters when using this reductant. Under our experimental conditions,

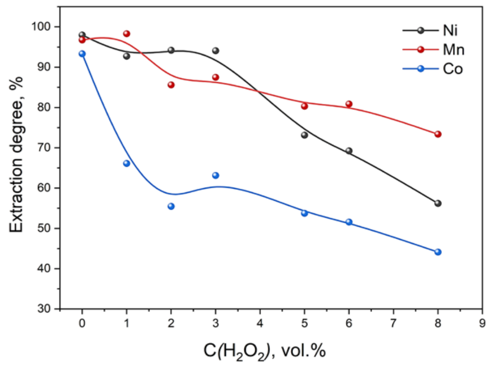

Fig. 4. Effect of hydrogen peroxide concentration on the extraction of Ni, Mn, and Co during leaching of NMC cathode mass (2 M malonic acid, 20 g/L, 60 °C, 90 min).

the addition of H_2O_2 likely promotes accelerated oxidative degradation of malonic acid and/or other side processes that offset any potential beneficial effect. This behavior may arise from concurrent mechanisms. At elevated H_2O_2 concentrations, oxidative degradation of malonic acid may be enhanced via radical pathways (potentially catalyzed by transition-metal species), leading to faster depletion of the effective leaching/complexing agent. In addition, at higher peroxide dosages, partial surface passivation and/or the formation of less soluble surface species cannot be excluded, which could further suppress metal dissolution.

Nevertheless, the results achieved without H_2O_2 indicate that malonic acid is capable of independently ensuring high leaching efficiency of NMC materials under properly selected conditions, which simplifies the technological scheme and reduces reagent consumption.

Thus, the optimal conditions for leaching spent NMC cathode mass with malonic acid include: an acid concentration of 2 M, a solid-to-liquid ratio of 20 g/L, a temperature of 60 °C, and a contact time of 80-90 min. Under these parameters, extraction of 98% nickel, 97% manganese, and 93% cobalt is achieved. The high extraction rates are ensured by the dual function of malonic acid: protonation of the oxygen sites of the oxide lattice promotes structural breakdown, while chelation of the released metal ions with the formation of stable six-membered rings stabilizes them in solution and shifts the equilibrium towards dissolution. The dissolved metals are present in solution predominantly as malonate complexes, specifically as $[M(\text{malonate})_n]^{2-2n}$ species (where $M = Ni^{2+}$, Co^{2+}, Mn^{2+}), which can be subsequently processed by conventional hydrometallurgical techniques such as selective precipitation, solvent extraction, or electrowinning to obtain high-purity metal salts or oxides.

4. Conclusion

In this study, a systematic investigation was conducted on the leaching of nickel, cobalt, and manganese from the spent cathode mass of NMC-type lithium-ion batteries using malonic acid. It was established that malonic acid acts as an effective standalone leaching agent without the need for external reducing agents such as hydrogen peroxide. Optimization of the process parameters revealed that the best results are achieved at a malonic acid concentration of 2 M, a solid-to-liquid ratio of 20 g/L, a temperature of 60 °C, and a contact time of 80-90 min. These conditions ensured extraction efficiencies of 98% for nickel, 97% for manganese, and 93% for cobalt from a material with a total content of 23.04 wt.% Ni, 3.07 wt.% Co, and 0.33 wt.% Mn.

The critical influence of temperature on process efficiency was identified: temperatures exceeding 60 °C lead to the thermal degradation of malonic acid via decarboxylation to form acetic acid, which significantly reduces the extraction yields of the target metals. It was experimentally demonstrated that the introduction of hydrogen peroxide into the system under the established optimal conditions not only fails to improve leaching efficiency but actually causes a decrease, likely due to the accelerated oxidative degradation of malonic acid or the occurrence of side reactions.

The high leaching efficiency is attributed to the dual function of malonic acid, which combines the ability to protonate oxygen sites in the oxide lattice with the formation of thermodynamically stable six-membered chelate complexes with transition metal ions, thereby shifting the equilibrium toward dissolution. The achieved extraction rates are comparable to those obtained using traditional mineral acids; however, the use of malonic acid eliminates the emission of toxic gases, reduces the corrosivity of the process, and ensures the biodegradability of the reagent. These results indicate the promise of malonic acid as an environmentally safe and technologically effective alternative to traditional inorganic acids in the hydrometallurgical recycling of spent lithium-ion batteries, opening avenues for developing more sustainable and eco-friendly technologies for closing the resource loop of critical metals.

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Извлечение никеля, кобальта и марганца из отработанных катодов NMC методом выщелачивания малоновой кислотой

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АННОТАЦИЯ

Настоящее исследование рассматривает возможность использования малоновой кислоты в качестве самостоятельного выщелачивающего агента для извлечения никеля, кобальта и марганца из катодной массы типа NMC без добавления внешних восстановителей. Проведена систематическая оптимизация параметров процесса выщелачивания, включая концентрацию кислоты, температуру, соотношение твердой и жидкой фаз и время контакта. Установлено, что оптимальные условия процесса составляют: концентрация малоновой кислоты 2 М, соотношение твердое/жидкое 20 г/л, температура 60 °С и время контакта 80-90 мин. При этих параметрах достигаются степени извлечения 98% для никеля, 97% для марганца и 93% для кобальта. Повышение температуры выше 60 °С приводит к снижению эффективности вследствие термического декарбоксилирования малоновой кислоты. Добавление перекиси водорода при оптимальных условиях не улучшает, а наоборот снижает эффективность извлечения. Высокая эффективность обусловлена двойной функцией малоновой кислоты, которая одновременно выступает агентом кислотного разрушения оксидной решетки и хелатирующим лигандом, стабилизирующим ионы металлов в растворе.

Ключевые слова: отработанные литий-ионные аккумуляторы, катодный материал NMC, гидрометаллургия, выщелачивание, малоновая кислота, переработка, зеленая химия.

Қолданыстан шыққан NMC катодтарынан никель, кобальт және марганецті малон қышқылымен шаймалау әдісі арқылы бөліп алу

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АҢДАТПА

Бұл зерттеуде малон қышқылын сыртқы тотықсыздандырғыштарды қоспай, NMC катодты пастасынан никельді, кобальтты және марганецті алу үшін дербес шаймалау агенті ретінде пайдалану мүмкіндігі қарастырылады.Қышқыл концентрациясын, температураны, қатты заттың сұйықтыққа қатынасын және жанасу уақытын қоса алғанда, шаймалау процесінің параметрлерін жүйелі түрде оңтайландыру жүргізілді. Процестің оңтайлы шарттары ретінде малон қышқылының концентрациясы 2 М, қатты/сұйық фазалар арақатынасы 20 г/л, температура 60 °С және жанасу уақыты 80-90 мин екені анықталды.Осы параметрлерде никель үшін 98%, марганец үшін 97% және кобальт үшін 93% деңгейіндегі бөлініп шығу дәрежесіне қол жеткізілді.Температураны 60 °С-тан жоғары көтеру малон қышқылының термиялық декарбоксилденуі салдарынан процестің тиімділігінің төмендеуіне әкеледі.Оңтайлы шарттарда сутек асқын тотығын қосу бөлініп шығу тиімділігін арттырмай, керісінше төмендетеді.Жоғары тиімділік малон қышқылының қосарлы функциясымен түсіндіріледі: ол бір мезгілде оксидтік торды қышқылдық бұзатын агент және ерітіндіде металл иондарын тұрақтандыратын хелаттаушы лиганд ретінде қызмет атқарады.

Түйін сөздер: қолданыстан шыққан литий-ионды аккумуляторлар, NMC катодтық материалы, гидрометаллургия, шаймалау, малон қышқылы, қайта өңдеу, жасыл химия.