



Closed-vessel microwave leaching of valuable metals from spent lithium-ion batteries (LIBs) using dual-function leaching agent: Ascorbic acid

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ABSTRACT

A novel closed-vessel microwave system for leaching of valuable metals from spent LIBs was examined using ascorbic acid. Important parameters and energy requirement were assessed. Leaching efficiency of Li, Co, and Mn and total energy requirement decreased as microwave heating rate increased from 5 °C/min to 90 °C/min. Leaching efficiency increased significantly with increasing acid concentration. Leaching rate of Li, Co, and Mn increased as temperature increased from 75 °C to 125 °C and data fitted well with pseudo second order model. Complete leaching of Li, Co, and Mn from spent LIBs was obtained at 0.5 M of ascorbic acid, 40 °C/min heating rate, 10 g/L of solid to liquid ratio, 125 °C within 10 min. Using 0.1 M of ascorbic acid could induce reduction of Co (III) in spent LIBs Co (II), as evidenced by XPS analysis. Total of 97.66% of Co and 58.99% of Mn in leaching solution were recovered on the addition of oxalic acid. Compared with conventional leaching, the closed-vessel microwave system provides an effective and energy-efficient leaching process since the heat loss is lessened and the high pressure and temperature of ascorbic acid solution intensified leaching reactions.

1. Introduction

End-of-life lithium-ion batteries (LIBs) are produced due to the rapid development and growth of electric vehicles and portable electronic devices. For decades, LIBs have been used for energy storage owing to their excellent electrochemical performances such as high energy and power density [1–3]. The amount of global spent LIBs is estimated to reach more than 11 million tons by 2030 [4]. Inappropriate disposal of spent LIBs may damage the environment since LIBs consist of toxic heavy metals such as cobalt (Co), manganese (Mn), and nickel (Ni), which can contaminate soil and groundwater [5,6]. Therefore, a sound management of spent LIBs is imperative to alleviate the growing environmental concerns [7]. The recycling of spent LIBs may also present an opportunity to recover the strategic elements and critical materials [8]. The cathode, anode, separator, and case of LIBs contain 5–20% of Co, 5–10% Ni, 5–7% lithium (Li), 5–10% copper (Cu), aluminum (Al), iron (Fe) and around 25% of plastics and organic compounds [9]. The recycle and recovery of valuable metals from spent LIBs is beneficial not only to the environment, but also to resource sustainability and economic benefits [10–12].

Metal recycling from spent LIBs can be divided into pretreatment,

metal-extraction, and purification. It is known that metal-extraction processes involving pyrometallurgy and/or hydrometallurgy play the key role in the whole recovery process [13]. State-of-the-art of valuable metal-extraction from secondary resource is to find the rapid, efficient and environmentally friendly process. Unlike pyrometallurgy with high energy consumption and emission of toxic gas, hydrometallurgy process is considered as the most promising method due to its high extraction yield, high purity of product, low energy consumption, and less gas emission [14,15]. Numerous studies investigated hydrometallurgy process to recover metals from spent LIBs using organic and inorganic acids as leaching agent [16,17]. However, hydrometallurgy process has drawbacks of the use of concentrated acid and long leaching time [18].

Process intensification is an alternative for valuable metals leaching from LIBs since both the energy and chemicals requirements can potentially be reduced during the process. Microwave-assisted extraction (MAE) is categorized as process intensification, which combines reactive extraction with rapid heating in advanced leaching process [19]. It has been proven that microwave could accelerate the heating process, which is induced by the ion collisions in the leaching solution. The MAE method has many advantages over conventional extraction process, including reduced amount of solvent, shortened heating time,

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and higher yields [20,21]. Shih et al. [22] reported effective leaching of valuable metals from LIBs using acids and 1% of H_2O_2 coupled with microwave heating. Some researches utilized microwave heating for reduction roasting in the pretreatment process to enhance water and acid leaching of valuable metals in spent LIBs [9,23]. The open-vessel microwave is preferred than the closed-vessel one due to higher sample loading and cheaper operational condition [24]. However, open-vessel microwave system suffers from high heat loss since the leaching solution will start boiling once temperature reaches boiling point [25]. Instead of boiling, pressurized water in the leaching solution of closed-vessel microwave system becomes subcritical when temperature is higher than 100 °C. And it has been demonstrated in our previous work that subcritical water extraction (SWE) resulted in efficient and effective leaching of valuable metals from LIBs [26]. There has been no research that examines the use of closed-vessel microwave extractor for spent LIBs.

Golmohammadzadeh et al. [27] reported that organic acids are efficient and eco-friendly leaching agents for metals recovery from spent LIBs since they also can act as chelating as well as reducing agents. Ascorbic acid is a natural water-soluble organic acid and known as vitamin C. It has been used as an effective leaching agent for valuable metals from spent LIBs and it was deemed as a mild reducing agent in several reports [28–30], yet, the role of ascorbic acid as a reducing agent is not fully proven and elaborated. In this study, leaching of Li, Co and Mn from spent LIBs cathode powder was conducted in a closed-vessel microwave system using ascorbic acid solution. Effects of microwave heating rate, acid concentration, and temperature were examined. Energy requirement was also assessed. Following leaching, the recovery of dissolved metals in leaching solution would be carried out by inducing oxalate precipitation, a simple and environmentally friendly method [31,32].

2. Experimental

2.1. Materials and method

Cathode powder of spent LIBs was obtained from the representative waste batteries treatment plant, Yen-Long Renewable Technology Co., Ltd. (Kaohsiung, Taiwan). It was subject to manual separation, discharging, crushing, screening, and roasting processes in the plant. When received, the pretreated cathode powder of spent LIBs was sieved through a 40-mesh screen, and stored for experiments. The leaching agent used was 99% of L(+)-ascorbic acid and the precipitation agent was 98% oxalic acid anhydrous purchased from Thermo Fisher Scientific Inc. (Acros Organic, Belgium). Concentrated hydrochloric acid (HCl, 37%) and nitric acid (HNO_3 , 65%) were purchased from Scharlab, S.L. (Spain). The ICP standard solutions of 1,000 mg/L of Li, Co, Mn, Ni, Cu, Fe and Al with purity >99% were purchased from Merck (Germany). All chemicals were used without any further purification.

2.2. Preparation and characterization of spent LIBs cathode powder

Elemental compositions in the spent LIBs cathode powder were analyzed by X-ray fluorescence spectrometer (XRF, Epsilon1, Malvern Panalytical, Malvern, UK), and the characterization of raw material and leaching residue was carried out by X-ray diffraction (XRD, D2Phaser, Bruker, Karlsruhe, Germany) at range 2θ from 10° to 90° with interval 0.05° and scan rate of 1°/min, scanning electron microscope (SEM, JSM-6390LV, JEOL, MA, USA) with acceleration voltage 0–30 kV equipped with energy dispersive spectrometer (EDS). The X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250, Thermo Fisher Scientific, Waltham, MA, USA) with a monochromatic X-ray gun at 15 kV and 200 W, beam size 650–120 μ m was used to assess the chemical states of elements of spent LIBs cathode powder after subject to ascorbic acid leaching. Total metals content in spent LIBs cathode powder was determined by aqua regia digestion method in which 3 g of LIBs cathode

Table 1
Results of XRF analysis of spent LIBs.

Metal (%)	Metal (%)	Metal (%)	Metal (%)
Co (62.655)	Fe (1.964)	Ca (0.151)	Ce (0.060)
Mn (11.267)	P (1.283)	S (0.148)	Ti (0.056)
Ni (5.795)	Cl (1.145)	Cd (0.104)	Zr (0.038)
Cu (4.440)	K (0.407)	La (0.106)	Sr (0.037)
Zn (3.442)	Si (0.240)	Rb (0.101)	Y (0.013)
Mg (3.028)	Eu (0.236)	Sn (0.095)	Nb (0.009)
Al (2.927)	Pb (0.176)	Nd (0.070)	Cr (0.007)

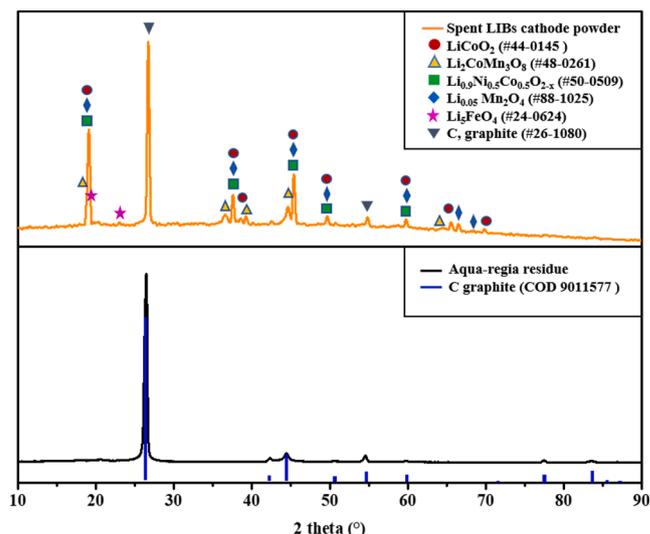


Fig. 1. XRD spectrum of spent LIBs and residue of aqua-regia digestion.

powder was mixed with 1:21:7 vol (mL) ratio of distilled water, concentrated HCl and HNO_3 , respectively. It was stirred for 16 h at room temperature followed by 2 h of heating at boiling condition. The digestion mixture was diluted to 250 mL, filtered, and then analyzed using inductively coupled plasma optical-emission spectrometry (ICP-OES, Thermo iCAP 7000, Thermo Scientific, Cambridge, UK). The major elements in the sample, Co, Li, Mn, Ni, Cu, Fe and Al, were detected at wavelength of 228.616 nm, 670.784 nm, 257.940 nm, 221.647 nm, 324.754 nm, 259.940 nm, and 309.271 nm, respectively. The digestion residue was dried at 50 °C for 3 d for further characterization.

From XRF results as shown in Table 1, Co is the most abundant metal (62.655%) in spent LIBs cathode powder, followed by 11.267% of Mn, 5.795% of Ni, 4.440% of Cu, 3.442% of Zn and others. However, XRF is limited by the atomic number of elements, and those with low atomic number and low energy, such as Li, carbon and oxygen could not be detected in XRF. The XRD spectrum of spent LIBs cathode powder (Fig. 1) illustrates that spent LIBs cathode powder is the mixture of some active cathode materials, including $LiCoO_2$, $Li_2CoMn_3O_8$, $Li_{0.9}Ni_{0.5}Co_{0.5}O_{2-x}$, $Li_{0.05}Mn_2O_4$, Li_2FeO_4 , and graphite. Total metal content of spent LIBs cathode powder from aqua regia digestion is shown in Table 2. The concentrations of Co, Mn and Li in spent LIBs cathode powder were 21.29%, 6.25% and 3.82%, respectively. The results from aqua regia digestion were used to determine the leaching efficiency of each metals. The digestion residue contained only graphite (carbon), constituting about 30% of spent LIBs cathode powder, implying complete dissolution of all metal content in the sample. The SEM images in Figure S1 demonstrate irregular shapes and varying size of the cathode powder particles before and after subject to aqua regia digestion (Figures S1a and S1c), while the EDS results show all metal content in cathode powder before and after aqua regia digestion (Figures S1b and S1d), and only graphite and zirconium (Zr) existed in the aqua regia residue (301.30 ± 5.23 mg/g) since they are inert compounds.

Table 2
Total metal content analyzed by aqua regia digestion.

Metal	Co	Mn	Li	Al	Ni	Fe	Cu
Content (mg/g)	212.90 ± 2.39	62.51 ± 0.16	38.22 ± 0.10	25.78 ± 0.56	22.70 ± 0.12	10.78 ± 0.29	10.43 ± 0.15

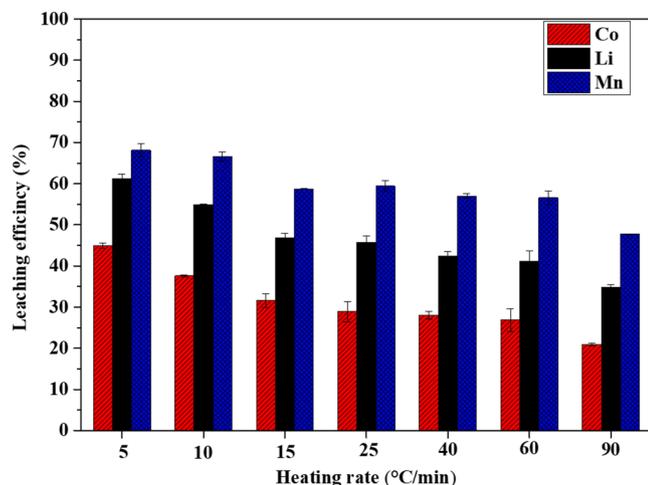


Fig. 2. Effect of heating rate on leaching efficiency of Co, Li and Mn at 0.2 M of ascorbic acid and solid concentration of 10 g/L.

2.3. Closed-vessel microwave-assisted leaching

The closed-vessel microwave-assisted leaching was carried out in the microwave digestion system (Start D, Milestone, Italy) as shown in Figure S2. It was equipped with a 100 mL cylindrical closed-vessel for high pressure and temperature, rotor segment, and control terminal to adjust the heating rate, desired temperature, and microwave irradiation time. Spent LIBs cathode powder and ascorbic acid were put into the vessel with 10 g/L of solid to liquid ratio. The vessel was sealed using tension wrench on the workstation and heated in microwave system with certain heating rate to the desired leaching temperature (75, 100, and 125 °C) and it was kept at constant temperature for specific period of time (0.5–30 min). Leaching time was not counted until reaching the desired temperature. After subject to leaching, the leaching mixture was filtered using 0.22 µm of membrane filter (Chrom Tech) to separate the leaching solution from residue. Metal content in the leaching solution was analyzed using ICP-OES to determine the leaching efficiency. The digestion residue was dried at 50 °C for 3 d for further characterization.

2.4. Metals recovery by precipitation

The recovery of valuable metals from leaching solution of spent LIBs cathode powder was conducted by precipitation with oxalic acid. The species distribution of Co and Mn precipitates was simulated by the MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms, MS-DOS versions, Stockholm, Sweden) as shown in Figure S3. It shows that cobalt oxalate (CoC₂O₄) would be precipitated at pH 0 to 10 (Figure S3a), while MnC₂O₄ precipitate forms at pH 1.7 to 10 (Figure S3b), with lower fraction compared to CoC₂O₄. The leaching solution with known concentration of Co, Li and Mn was mixed with oxalic acid anhydrous, at two times the stoichiometric concentration, stirred for 5 min, and then let it settle over night at room temperature. The precipitates were collected using vacuum filtration with membrane filter 0.2 µm (Advantec), dried at 105 °C for 3 h, and then characterized by XRD and SEM-EDS, while the filtrate was analyzed by ICP-OES to determine the residual metal content.

Table 3
Energy consumption at various microwave heating rate.

Heating rate (°C/min)	Average power (W)	Total energy (J)
5	111.5	107,054
10	137.2	65,877
15	162.3	51,951
25	229.7	43,640
40	321.4	36,965
60	474.0	35,551
90	587.2	29,362

3. Results and discussion

3.1. Heating rate and microwave power

The effects of heating rate and microwave power on leaching efficiency were studied using 0.2 M of ascorbic acid at 10 g/L of solid to liquid ratio. The heating rate was varied at 5, 10, 15, 25, 40, 60, and 90 °C/min, respectively, to reach 100 °C, then the leaching mixture was immediately filtered to stop the reaction. It took 50 s to reach 100 °C when heated at 90 °C/min with maximum microwave power of 600 W. Higher heating rate results in shorter heating time. The effect of heating rate on leaching efficiency of Co, Li, and Mn can be seen in Fig. 2. The leaching efficiency of Co, Li and Mn decreased gradually from 44.9% of Co, 61.20% of Li, and 68.10% of Mn to 28.07% of Co, 42.48% of Li and 57.02% of Mn as the heating rate increased from 5 °C/min to 40 °C/min, and it decreased further as heating rate increased to 90 °C/min. It was probably due to shorter reaction time for higher heating rate. The microwave power profile during closed-vessel microwave leaching at each heating rate is shown in Figure S4. Higher heating rate required higher microwave power. In general, the initial microwave power requirement was high, it then decreased sharply, followed by gradual increase during closed-vessel microwave leaching process. It demonstrated that microwave heating is a non-linear process which starts inside through outside and the microwave energy was absorbed by the particles and the intramolecular interaction [33]. The average energy consumption was estimated using the empirical equation in which Watt is equal to Joule per second, the integral of power profile (Figure S4) during microwave

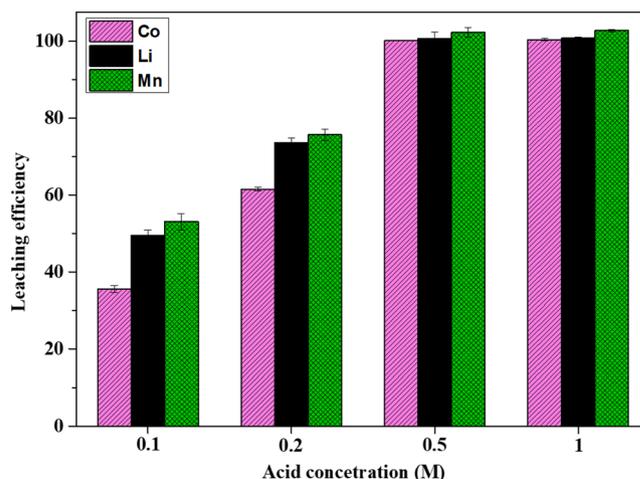


Fig. 3. Effect of acid concentration on microwave leaching at 125 °C and solid concentration of 10 g/L for 10 min.

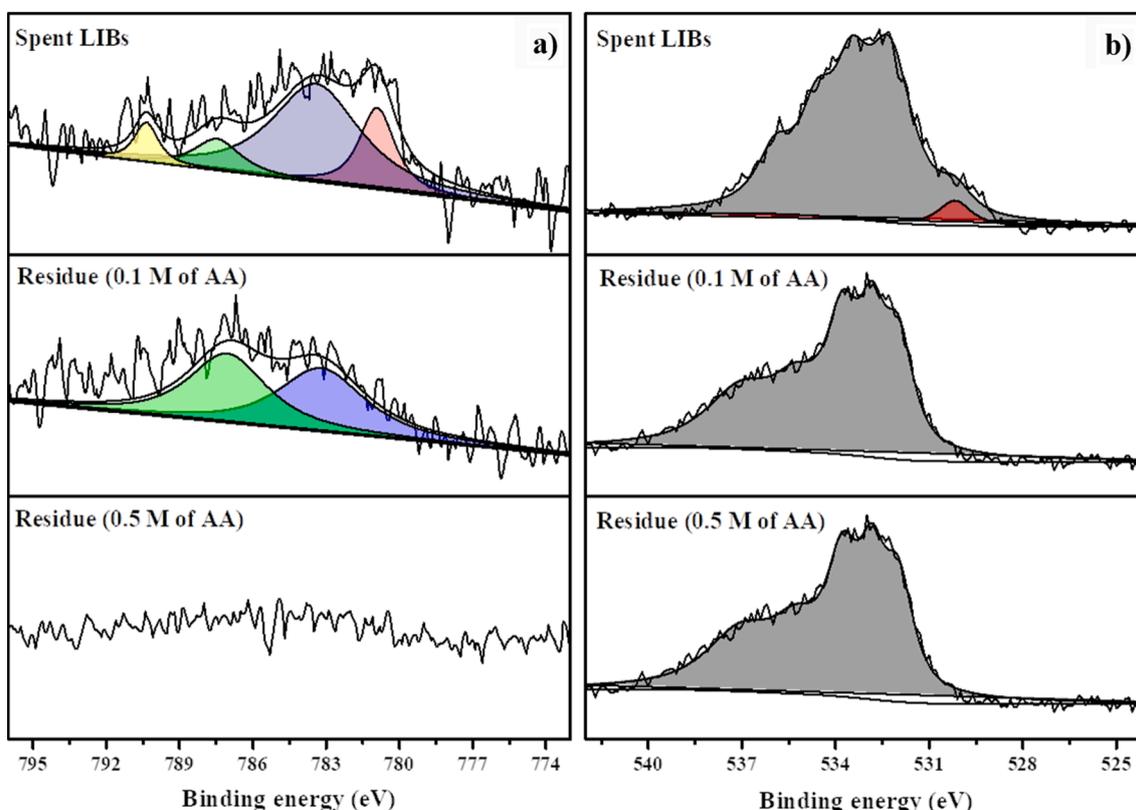


Fig. 4. XPS spectrum of a) Co $2p_{3/2}$ and b) O 1 s.

leaching resulted energy consumption of each heating rate shown in Table 3. Increasing the heating rate could reduce the energy consumption of microwave due to the shorter heating time. However, leaching efficiency decreased with increasing heating rate as well. There is trade-off between leaching efficiency and total energy requirement, and 40 °C/min was chosen as the microwave heating rate for further experiments.

3.2. Effect of ascorbic acid concentration and leaching mechanism

The effect of ascorbic acid concentration on the leaching efficiency of Co, Li, and Mn was investigated using 0.1 M, 0.2 M, 0.5 M and 1 M of ascorbic acid in closed-vessel microwave system at 125 °C for 10 min. The initial pH values of 0.1 M to 1 M ascorbic acid solutions ranged from 2.65 to 2.05, respectively. It is noted that pH values were lower than the deprotonation constants (pK_{a1} of 4.10 and pK_{a2} of 11.6), therefore ascorbic acid is still mostly in molecular form in the leaching solution. Fig. 3 shows the significant rise of leaching efficiency of Co, Li, and Mn from 35.55% to 61.51%, 49.47% to 73.59%, and 53.03% to 75.67%, respectively, as ascorbic acid concentration increased from 0.1 M to 0.2 M. Ascorbic acid solution consists of polar molecules (mainly water molecules) which could well absorb the microwave energy and produce heat by in-situ energy conversion [30]. The oscillating electric field from microwaves induced the alignment of polar molecules and resulted in a fast heating [34]. Dipolar molecules of ascorbic acid in leaching solution play the key role in the dipole rotation process under microwave irradiation that leads to intensive thermal gradient [35]. The higher the concentration of dipolar molecules, the more intensive the dipole spinning in the leaching solution under microwave irradiation, which promoted rapid heating and vigorous molecular collisions. Ascorbic acid of 0.5 M was sufficient to completely leach out Li, Co, and Mn (100% leaching efficiency) from spent LIBs cathode powder with 10 g/L of solid to liquid ratio at 125 °C within 10 min.

Ascorbic acid played dual roles as the acid agent and the reducing

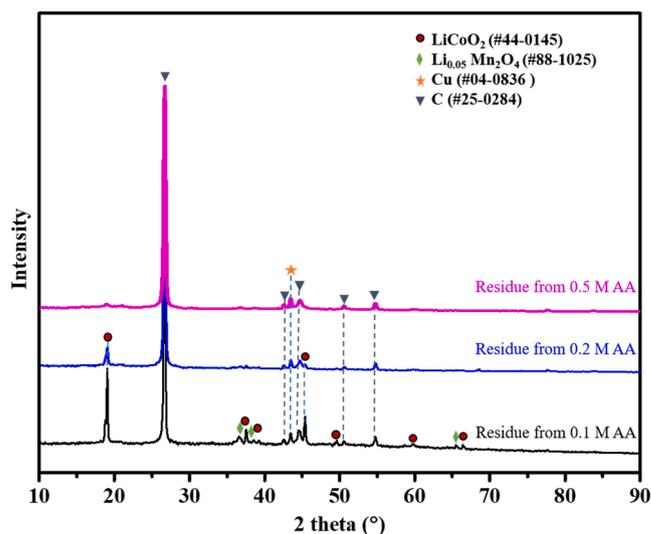


Fig. 5. XRD spectrum of leaching residues using ascorbic acid at different concentration.

agent that facilitated the leaching of Co and Mn from spent LIBs cathode powder. Our previous study showed the XPS analysis that Co (III) in spent LIBs cathode powder was completely converted to more soluble Co (II) by ascorbic acid but not by HCl [26]. In this study, we examined the redox mechanism of Co by XPS analysis of leaching residue of cathode powder using ascorbic acid of two different concentrations (Fig. 4). Peaks of Co $2P_{3/2}$ in Fig. 4a show that spent LIBs cathode powder contained both Co (III) and Co (II) at 780.9 and 783.4 eV, respectively, with satellite peaks at 787.5 and 790.4 eV that correspond to Co (III) and Co (II) excitation. Peaks of Co $2P_{3/2}$ of leaching residue using 0.1 M of ascorbic acid revealed that only Co (II) content was detected at 783.2 eV

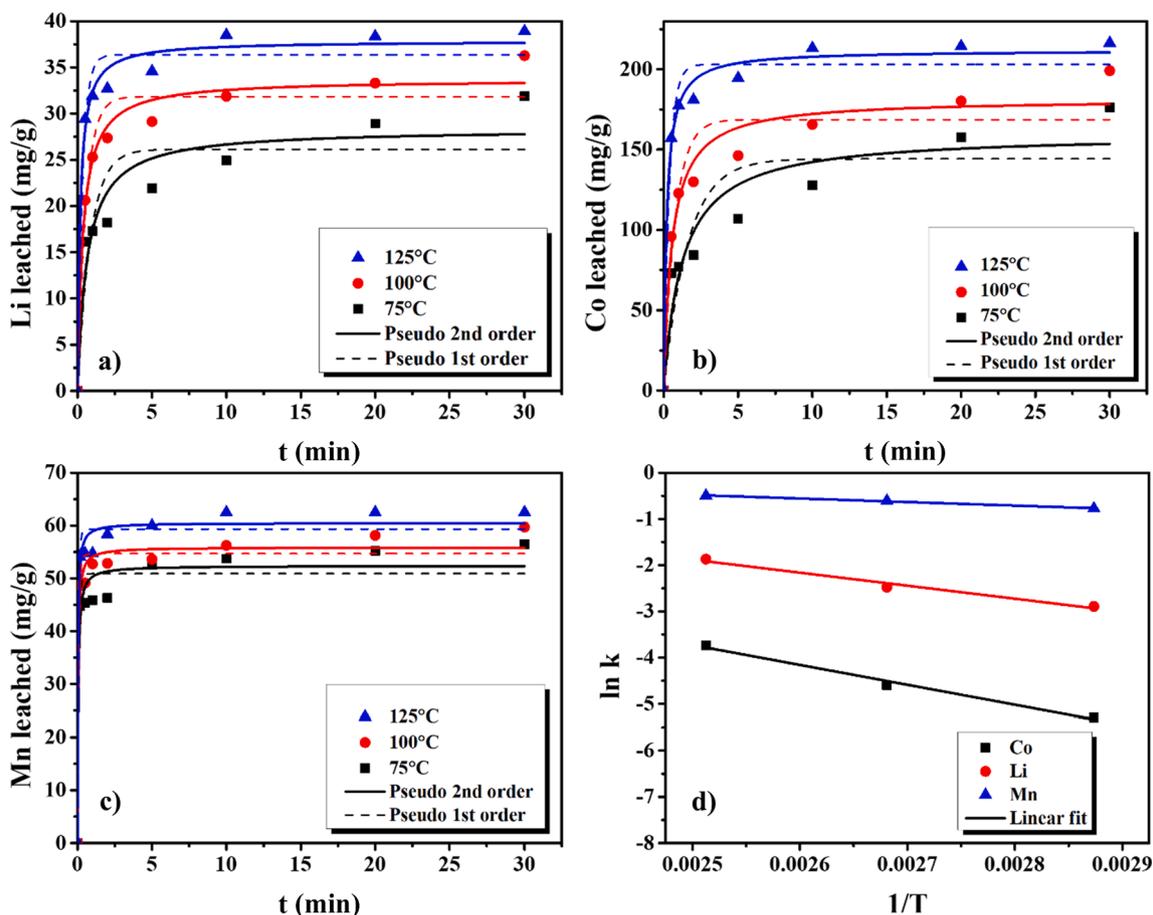


Fig. 6. Kinetic study of a) Co, b) Li, and c) Mn leaching and d) Arrhenius plot.

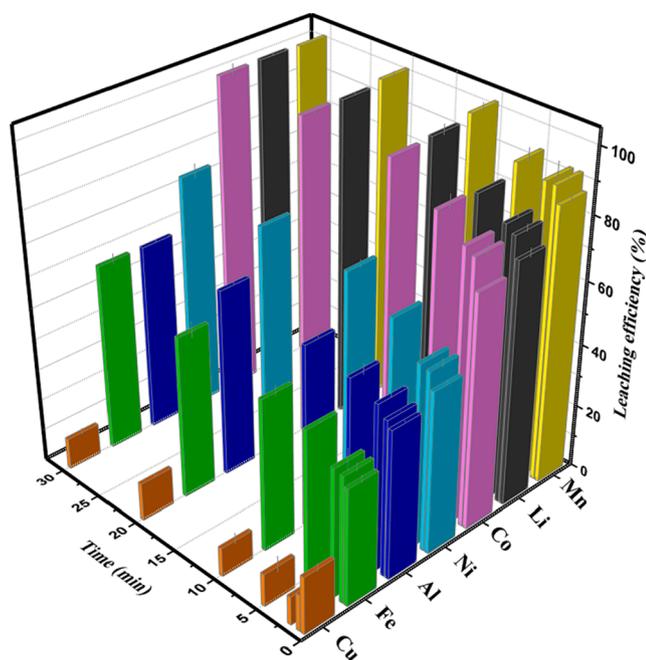


Fig. 7. Leaching efficiency of metals using 0.5 M of ascorbic acid at 125 °C in closed-vessel microwave system.

with satellite peak at 787.1 eV. Therefore, it confirmed that Co (III) was reduced to Co (II). When the concentration of ascorbic acid increased from 0.1 M to 0.5 M, Co was completely leached out from spent LIBs

cathode powder. Fig. 4b confirmed that LiCoO₂ peak (530.3 eV) of spent LIBs cathode powder disappeared when it was subjected to 0.1 M and 0.5 M of ascorbic acid solution. Complete leaching of valuable metals was achieved using 0.5 M of ascorbic acid in closed-vessel microwave system at 125 °C for 10 min with heating rate 40 °C/min. Fig. 5 shows the XRD spectra of leaching residues using 0.1 M, 0.2 M, and 0.5 M of ascorbic acid. It confirmed that more LiCoO₂ leached out when using more concentrated ascorbic acid. The XRD spectra of leaching residue using 0.5 M of ascorbic acid showed that leaching of LiCoO₂ and Li_{0.05}Mn₂O₄, was complete and only graphite (carbon) was found in the residue. It is noted that trace amount of Cu was detected in the leaching residue. It could be attributed to the reduction of dissolved Cu(II) to elemental Cu in ascorbic acid solution [36].

3.3. Effect of temperature and leaching kinetics

The effect of temperature and leaching kinetics of Co, Li, and Mn by closed-vessel microwave was examined at 75 °C, 100 °C, and 125 °C, respectively, using 0.5 M of ascorbic acid with solid to liquid ratio of 10 g/L. Samples were taken for analysis at certain period of time, ranging from 0.5 min to 30 min. Leaching efficiency of Li, Co, and Mn as affected by reaction time at three different temperatures are shown in Fig. 6. The equilibrium conditions of Li and Co were achieved after 10 min leaching, while shorter reaction time of 5 min was needed for Mn. It is noted that minor elements, such as Ni, Al and Fe were also leached out, with maximum leaching efficiency of 75.85%, 59.60% and 59.72%, respectively, as shown in Fig. 7. For 2 min of reaction time at 75 °C, leaching efficiency of Li, Co, and Mn were 47.65%, 39.63%, and 79.14%, respectively, and it increased to 71.56%, 61.05%, and 86.06% at 100 °C, and 85.57%, 85.03%, and 92.12% at 125 °C. Higher leaching

Table 4
Kinetic parameters of Li, Co and Mn leaching using 0.5 M of ascorbic acid.

Metal	Temp (°C)	Pseudo first order			Pseudo second order		
		Ce	k	R ²	Ce	k	R ²
Li	75	26.13	1.1571	0.8095	28.35	0.0555	0.9016
	100	31.83	1.7709	0.9400	33.70	0.0839	0.9778
	125	36.35	2.9675	0.9460	37.86	0.1542	0.9854
Co	75	144.24	0.6273	0.7797	159.93	0.0050	0.8804
	100	168.71	1.2998	0.8926	181.58	0.0101	0.9539
	125	203.09	2.6646	0.9637	211.90	0.0239	0.9890
Mn	75	50.89	12.4727	0.9350	52.38	0.4617	0.9570
	100	54.67	13.0081	0.9668	55.88	0.5439	0.9805
	125	59.35	14.3650	0.9733	60.49	0.6090	0.9841

Table 5
Comparison of different leaching processes for LIBs.

Leaching solution	Leaching conditions	Results	References
1 M H ₂ SO ₄	40 °C, 30 g/L, 60 min	80% of Li, <40% of Co, Mn, Ni	[40]
2 M H ₂ SO ₄ + 3 vol% of H ₂ O ₂	60 °C, 50 g/L, 60 min	>99% of Li, Ni, Co, Mn	[41]
1.5 M H ₂ SO ₄ + 0.25 M ascorbic acid	60 °C, 15 mL/g, 60 min	>99% of Li, Ni, Co, Mn	[29]
1.5 M lactic acid	70 °C, 20 g/L, 30 min	33.22% of Ni, 33.63% of Co, 30.72% of Mn, and 59.34% of Li	[42]
1.25 M citric acid + 1 vol% of H ₂ O ₂	*Microwave (600 W): 100 °C, 25 g/L, 20 min Ultrasound (60–120 W): 60 °C, 25 g/L, 60 min	~100% of Co ~80% of Co	[22]
Chlorinated polyvinyl chloride (CPVC)	Subcritical water: 250 °C, 30 mL/g, 60 min	98.71% of Li, 97.69% of Co	[43]
Citric acid 0.4 M	Continuous hydrothermal at 200 °C, 10 g/L, 30 mL/min for 60 min	81.3% of Li and 92.7% of Co	[44]
0.5 M ascorbic acid	**Microwave: 125 °C, 40 °C/min, 10 g/L, 10 min **Microwave: 75 °C, 40 °C/min, 10 g/L, 10 min	100% of Li, Co, Mn 65.21% of Li, 60.10% of Co, 85.95% of Mn	This study

*Atmospheric-pressure (open-vessel) microwave.

**Closed-vessel microwave.

temperature resulted in increased leaching efficiency of Li, Co and Mn. The ascorbic acid solutions inside the closed-vessel microwave vessel approached subcritical condition, as characterized by temperature above the atmospheric boiling point of water (100 °C, 0.1 MPa) but below the critical point of water (374 °C, 22.1 MPa). Pressurized water at higher temperature induces an increased movement/rotation, diffusivity, and mass transfer of water molecules, all beneficial to extraction [37]. In conventional subcritical water extraction (SWE), more than 95% of Co, Li, and Mn were leached out from spent LIBs using 0.2 M of ascorbic acid within 30 min at 100 °C (Lie et al., 2020). However, it took 30–40 min for heating in SWE. For comparison, heating step in the use of closed-vessel microwave system was rapid that could be completed within short period of time.

The kinetic data of Li, Co, and Mn leaching from spent LIBs cathode powder at different temperature were fitted using pseudo first order and pseudo second order models. It was found that pseudo second order model could describe the reaction kinetics better. The leaching rate constants of Co, Li and Mn increased as temperature increased as shown in Table 4. It was because high temperature induced high chemical

reaction rate and diffusion rate which enhanced the leaching efficiency [38]. Arrhenius law was used to determine the activation energy of Li, Co, and Mn leaching by plotting ln(k) vs. 1/T as shown in Fig. 6d. The activation energy of 35.70 kJ/mol, 23.41 kJ/mol, and 6.39 kJ/mol for Co, Li and Mn was found, respectively. It was proposed that leaching processes of Li and Co were controlled by chemical reaction, while Mn leaching process was controlled by diffusion judging from the activation energy values [39].

3.4. Comparison of leaching processes

The performance of valuable metals leaching from spent LIBs cathode powder using various methods was summarized in Table 5. In conventional leaching, it has been demonstrated that <40% of Co, Mn, and Ni were leached out using 1 M of H₂SO₄ with 30 g/L of solid to liquid ratio at 40 °C in 60 min [40]. When using 2 M of H₂SO₄ and 3% H₂O₂ of 50 g/L at 60 °C, >99% of metals were leached out in 60 min [41]. Very effective leaching (>99%) of Li, Ni, Co, and Mn was observed when using 1.5 M of H₂SO₄ and 0.25 M of ascorbic acid at 60 °C, 15 mL/g, in 60 min [29]. If only 1.5 M of lactic acid was used, limited leaching was found for Ni (33.22%), Co (33.63%), Mn (30.72%), and Li (59.34%) [42]. It shows that reducing agent is essential for Co, Mn and Ni leaching when using inorganic acid, while organic acid may not be very effective when used alone. Shih et al. [22] showed that 100% of Co could be leached out using open-vessel microwave at 600 W, 100 °C, 25 g/L, in 20 min, and ca. 80% of Co was leached out using microwave or ultrasound at 60–120 W, 60 °C, 25 g/L, in 60 min. When using subcritical water in the presence of chlorinated polyvinyl chloride (CPVC) at 250 °C and 30 mL/g, 98.71% of Li and 97.69% of Co were leached out in 60 min [43]. The very recent work by Zheng et al. [44] showed that the continuous hydrothermal process with greener leaching agent, mild concentration of citric acid, is feasible to be applied in practice, however, high temperature and long leaching time are unfavourable for waste recovery since it required high operational cost and energy.

As demonstrated in the current work, 65.21% of Li, 60.10% of Co, and 85.95% of Mn was leached out in 10 min at 75 °C, while complete leaching of Li, Co, and Mn could be obtained at 125 °C in 10 min. It is apparent that closed-vessel microwave system could accelerate and enhance leaching process significantly. Not just heat loss is lessened, closed-vessel microwave system also rendered high temperature (>100 °C) and pressure (>1 bar) conditions of ascorbic acid solution possible. And the subcritical water condition enhanced metals extraction owing to decreased solvent viscosity and enhanced mass transfer [26,45]. That was probably why 0.5 M of ascorbic acid alone could induce complete leaching of Li, Co, and Mn from spent LIBs cathode powder. The process is efficient, effective, and energy-efficient since ascorbic acid at mild concentration of 0.5 M could leach out all valuable metals at modest temperature of 125 °C within relatively short reaction time of 10 min. Of course, there are disadvantages of the system, such as higher capital cost of the pressurized reactor and safety risks of high operational condition (T and P). However, the closed-vessel microwave

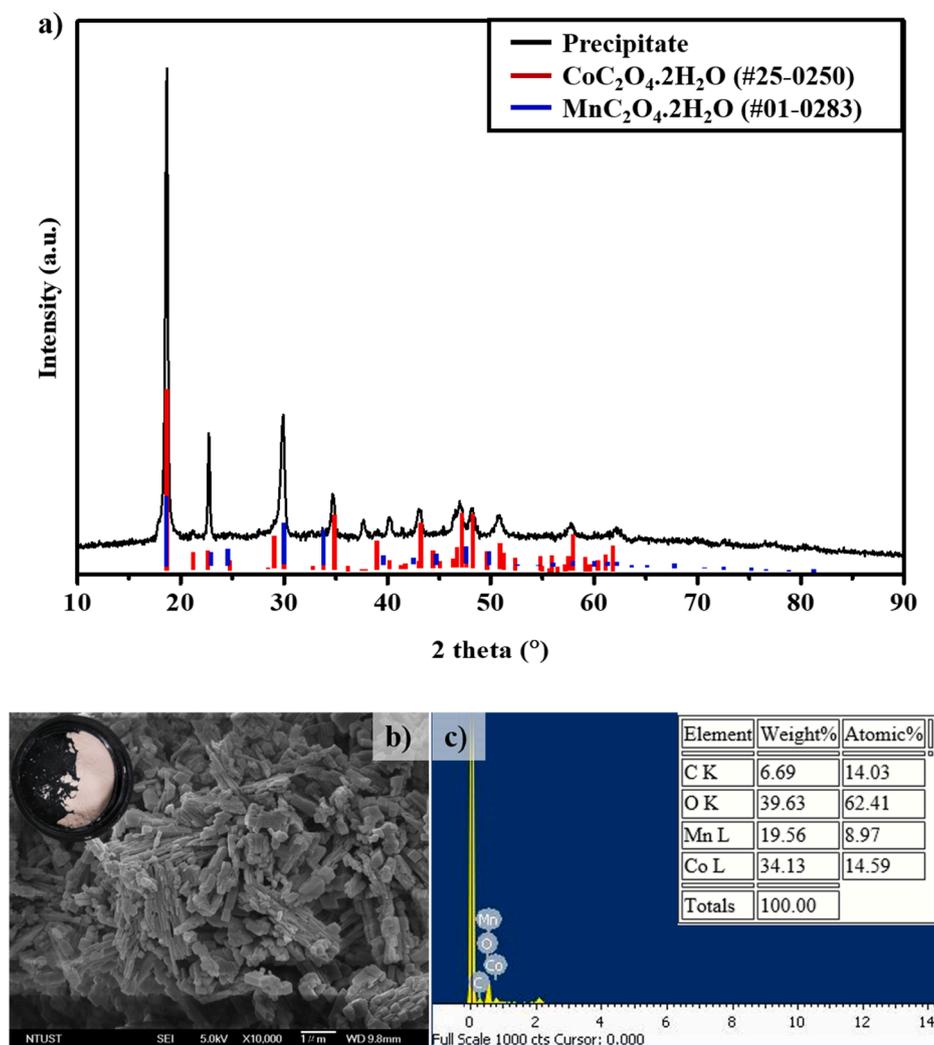


Fig. 8. Characterization of recovery products by a) XRD, b) SEM, and c) EDS.

system is full of potential and deserves further study on industrial application for leaching of valuable metals from spent LIBs.

3.5. Recovery of valuable metals

The recovery of Co and Mn was conducted by precipitation at room temperature, in which the leaching solution from closed-vessel microwave system was mixed with oxalic acid. The pH value changed from 3.70 of the leaching solutions to 2.61 of the supernatants after subject to precipitation and filtration. It was found that 97.66% of Co and 58.99% of Mn precipitated with oxalic acid, while Li could not form precipitates. Those results are in agreement with the thermodynamic modeling by MEDUSA, which predicts 100% precipitation of Co and 55% of Mn at pH 2.6. The pink powder was obtained as the recovery products. Fig. 8a shows the XRD pattern of recovery products and it confirmed that the precipitates mostly were cobalt oxalate dihydrate ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) with JCPDS 25-0250 and manganese oxalate dihydrate ($\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) with JCPDS 01-0283. The SEM image of precipitate could be seen in Fig. 8b that shows the nano-rod shape crystal of the recovery products. From EDS analysis (Fig. 8c), it confirmed the dominant elements in precipitate were Co, Mn, C, and O, which could attribute to $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. It is noted that the mixture of these compounds are potential high-performance flexible solid-state asymmetric supercapacitors in the field of high-energy-density energy storage devices [46].

4. Conclusions

It was shown in the current study that closed-vessel microwave system could achieve 100% leaching of Li, Co, and Mn from spent LIBs cathode powder within 10 min using 0.5 M of ascorbic acid of solid to liquid ratio 10 g/L, at 125 °C. Important parameters, such as acid concentration and temperature were examined. Pseudo second order model could well describe the leaching of Li, Co, and Mn from spent LIBs cathode powder in closed-vessel microwave. The reduction of Co(III) to Co(II) by ascorbic acid at different concentrations was analyzed by XPS that highlighted the role of ascorbic acid, even at as low concentration as 0.1 M, in inducing leaching of metals from spent LIBs cathode powder. The recovery of Co and Mn was conducted using oxalic acid to produce form oxalate precipitates. From the comparison with various works, it is proposed that closed-vessel microwave system is an alternative technology full of potential for efficient and effective leaching of valuable metals from spent LIBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2021.118458>.

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