

Recovery of Graphite from Lithium Ion Batteries Leaching using Sulfuric Acid as Anode Materials

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Abstract

Used lithium-ion battery can be recycled and reused as a new battery component. Separation of graphite by mechanical method was carried out to remove plastic components. The graphite obtained was washed using dimethyl carbonate (DMC) and N-methyl-2-pyrrolidone (NMP) and leached in H₂SO₄. The residue obtained was heated in furnace at 500°C for 1 hour using N₂ atmosphere. FTIR and XRD characterizations were carried out to compare anode materials that obtained by mechanical process only and by leaching process. The FTIR characterization showed that DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite did not show any significant differences in term of their functional groups. XRD results indicated that the residue that obtained were graphite that in accordance with JCPDS 96-901-2231. The 2θ diffraction peaks of DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite were at 26.37°, 26.32° and 26.33°, respectively. The diffractogram peak of LiMn₂O₄ impurities in spent graphite at 18.70°, was no longer appears on the treated graphite. It is because the LiMn₂O₄ has dissolved in the sulfuric acid. SEM images of washed graphite and leached graphite show similar morphology. The graphite obtained has the potential to be reused as anode material for new lithium-ion battery.

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1. Introduction

Lithium ion batteries have advantages in term of temperature tolerance, lifetime, and energy density [1]. LIB is considered as the most promising energy storage medium due to lithium's small molecular weight and electropositive properties [2]. The increase of lithium ion batteries demand has led to an increase in battery production. Lithium ion batteries sales in electric vehicles increase from 5 million in 2015 to 7 million in 2020, will reach 180 million in 2045 [3]. On the other hand, the used LIB wastes can cause serious environmental problem if they were directly discharged into the environment. The fluorinated compounds contained in the electrolyte of used batteries poses a risk to the environment [4]. Recycling and reuse of anode materials has not attracted much attention because of the lower added value of precious metals and the difficulty of regeneration. However, considering the rapid increase in the number of used Li-ion batteries, it is believed that effectively recycled anode materials can also bring considerable economic benefits and realize the sustainable development of the lithium-ion battery industry [5]. Lithium ion batteries consist of various components with different chemical properties, including aluminum cathode and copper anodes, activated carbon and transition metal oxides active materials [6]. The recycling of materials, such as graphite, lithium iron phosphate, and lithium manganese oxide have been carried out using physical, chemical, and biological methods. Physical methods are usually applied as a pre-treatment to separate the outer container and collect metal components that will undergo chemical treatment (hydrometallurgy or pyrometallurgy) or biological treatment. However, chemical and biological treatment products are difficult to purify because of the presence of organic materials in lithium ion batteries such as graphite, electrolytes, PVDF binders which could inhibit chemical reactions [7]. Graphite and other negative electrode materials in pyrometallurgical recycling are fed into the smelting furnace together with the positive electrode. This causes only metallic materials to be recovered [1]. Many previous studies have carried out leaching lithium ion batteries with acid as a leaching agent such as HNO_3 , H_2SO_4 , ascorbic acid, and L-aspartic acid. The results showed the recovery of valuable materials with efficiency >95% Li and Co (HNO_3), 100% Li and 95% Co (H_2SO_4), 98.5% Li and 94.8% Co (ascorbic acid), 60% Li and Co (L-aspartic acid) [8]–[11]. However, the leaching carried out by previous studies still focuses on the leaching of battery cathode materials. Therefore, in this study, the mechanical separation of the lithium ion battery from the laptop battery was carried out and followed by a purification process to remove the influence of binders and solvents on the anode. Purification was carried out through a washing process with DMC and NMP, followed by the leaching process of battery anode material with $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ to purify graphite that obtained.

2. Experimental

2.1. Materials and Instrument

The materials used in this study i.e. spent lithium ion batteries, sulfuric acid (Merck) as leachate, and H_2O_2 (Merck) as the reductant. NMP (N-methyl-2-pyrrolidone) 99.5% from Sigma Aldrich, DMC (Dimethyl carbonate) 99% from Merck were used in material washing. The instruments used were XRD (X-Ray Powder Diffraction, PANalytical Xpert MPD) and FTIR (Fourier Transform Infrared Spectrometer, Shimadzu 8400S).

2.2. Recycling of Anode Material

Procedure of the present work was illustrated in Fig. 1. The anode material from spent lithium ion battery was used. The battery was disassembled mechanically and separated from its outer plastic layer. The battery cells were immersed in NaCl 5% solution for 24 hours and dried in air. Then, the anode materials were scraped slowly to separate it from the foil. The spent anode materials were washed twice with 30 mL of DMC and NMP to dissolve the

remaining electrolyte and binder in the anode material [1], then dried at a temperature of 100°C. The anode materials were leached in H_2SO_4 2 M and H_2O_2 4% with a liquid:solid ratio (L:S) of 10:1 for 120 minutes at 70°C. Stirring speed was set at 250 rpm to obtain good mass transfer. Filtration was carried out to separate the anode material from leachate and washed with water to pH 6-7. The solvent then evaporated at 500°C for 1 hour using N_2 atmosphere [12].

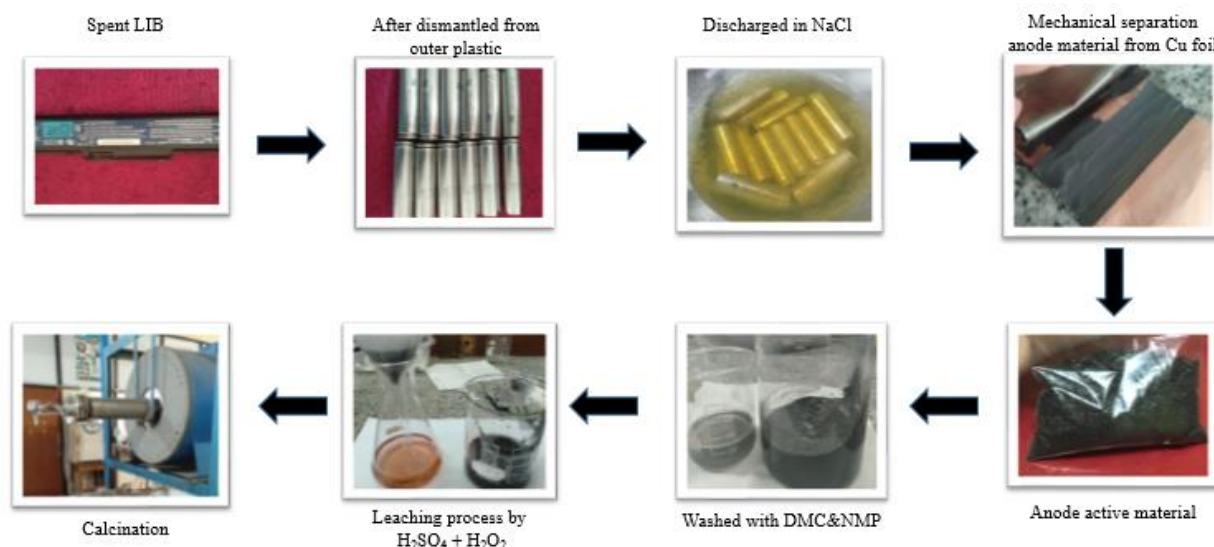


Figure 1. The process of disassembling and recycling anode active material from spent lithium ion batteries

2.3. Characterization

2.3.1. FTIR Characterization

FTIR Characterization was carried out to determine whether there were differences in functional groups of spent graphite, DMC and NMP washed graphite, H_2SO_4 and H_2O_2 leached graphite. Characterization with the FTIR was carried out in the wavelength range of $4000\text{--}400\text{ cm}^{-1}$. The sample was ground with the addition of KBr in an agat mortar. The mixture was placed in a mold and hydraulically pressed to form pellets. The pellet was placed in the sample holder for FTIR analysis [13].

2.3.2. XRD Characterization

The crystal structure of anode materials were characterized using XRD (X-Ray Powder Diffraction). The samples were measured using Cu $\text{K}\alpha$ radiation source ($\lambda = 1.5406\text{\AA}$), voltage 40 kV, current of 30 mA, the scan step time used was 10.15 seconds, and measured at an angle of $5^\circ \leq 2\theta \leq 100^\circ$ [14].

2.3.3. SEM Characterization

The morphology of anode material can be known through SEM characterization. The samples were placed in the sample holder, then coated with gold on the sample surface (coating stage). The samples were put into a vacuum and analyzed using SEM.

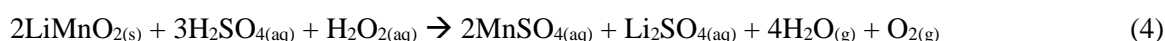
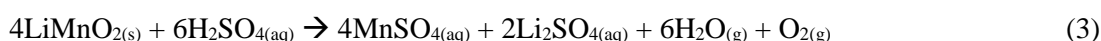
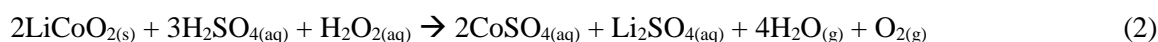
3. Results and discussion

3.1. Leaching on Material

The direct mechanical separation of anode materials, generally, consists of a current collector (copper foil), active material (graphite), conductive additive (acetylene black) and binder. Graphite is coated on a copper foil surface with

a polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) binder [15]. The anode material was washed with the solvent to remove the polymer electrode binder from the active electrode material. DMC and NMP was used to remove polymeric binder in graphite [1], [16]. In order to regenerate graphite, copper and aluminum was removed. Aluminum and copper was leached from spent graphite by hydrochloric acid or sulfuric acid [15]. In this study, sulfuric acid was used as a leaching agent and H_2O_2 was used as a reductant. H_2O_2 was added in order to convert cobalt ions to the +2 state. The leaching conditions was carried out using H_2SO_4 2 M, H_2O_2 4%, S/L ratio of 1:10, during 2 hours, and the temperature was 70° [12].

The following chemical equation (1), (2), (3), and (4) represents the dissolution of used LIB (such as the types of LiCoO_2 and LiMnO_2) in H_2SO_4 solution without and in the presence of H_2O_2 solution [12].



3.2. FTIR Spectra of Anode Active Materials

Spent graphite, DMC and NMP washed graphite, and $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ leached graphite were characterized by FTIR (Fourier Transform Infrared Spectrometer) to compare their functional groups. The results of the FTIR spectrum were shown in Fig. 2. The FTIR spectrum of the anode material in the samples did not show a significant difference. These materials generally have the same functional groups as presented in Table 1.

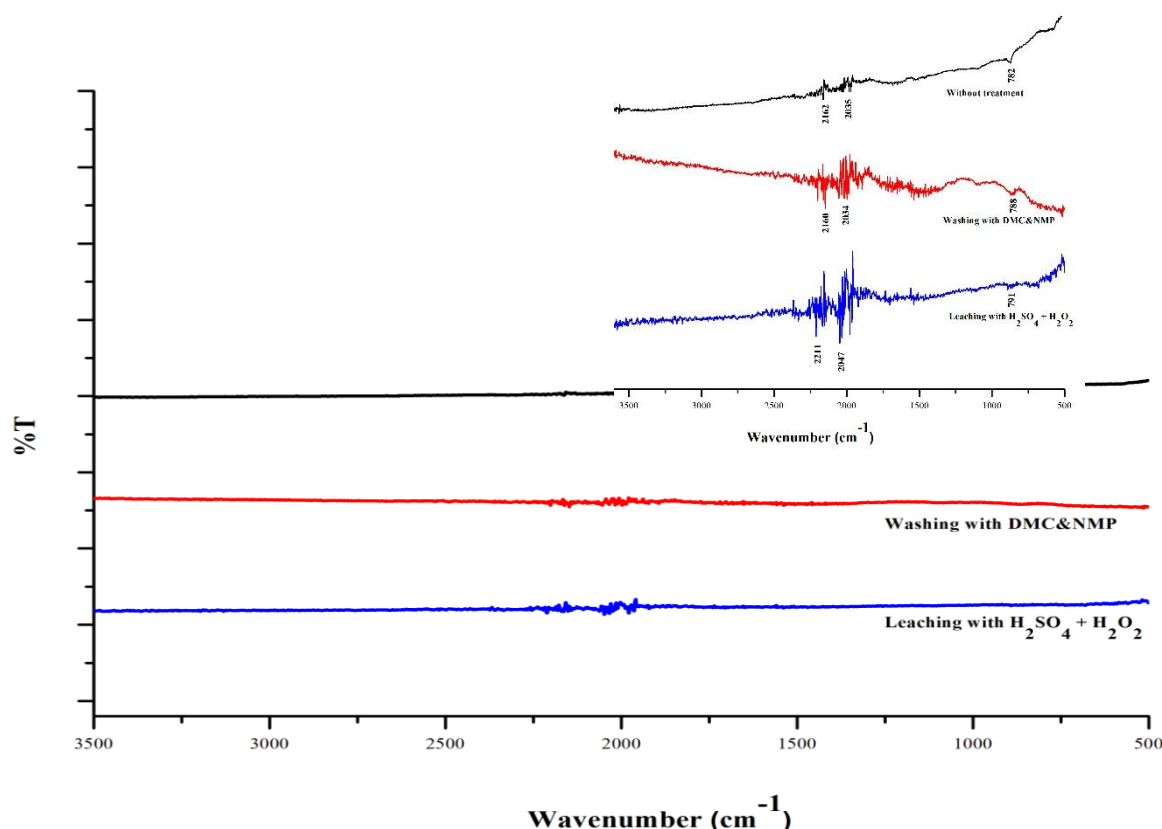


Figure 2. FTIR spectra of spent graphite, DMC and NMP washed graphite, H_2SO_4 and H_2O_2 leached graphite

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Table 1. Table FTIR spectra of spent graphite, DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite

Sample	Wavenumber (cm ⁻¹)	Functional Group	Reference
Spent Graphite	2162	C≡C alkyne	[17]
	2035	C=C=C stretching	[18]
	782	CH ₂ bending (long-chain band)	[17]
Washed Graphite	2160	C≡C alkyne	[17]
	2034	C=C=C stretching	[18]
	788	CH ₂ bending (long-chain band)	[17]
Leached Graphite	2211	C≡C alkyne	[17]
	2047	C=C=C stretching	[18]
	791	CH ₂ bending (long-chain band)	[17]

Fig. 2 indicated that the absorption of functional groups in the material has relatively low intensity. This is in accordance with the characteristics of the graphite absorption band at [19] where stretching is not interpretively useful because many weak absorption peaks appear. As written in Table 1, the possible FTIR absorption band that appears is the C≡C alkyne, C=C=C stretching, CH₂ bending (long-chain band) vibration.

3.3. Diffractogram of Anode Active Materials

Spent graphite, DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite were characterized using XRD. The diffractogram that obtained was shown in Fig. 3.

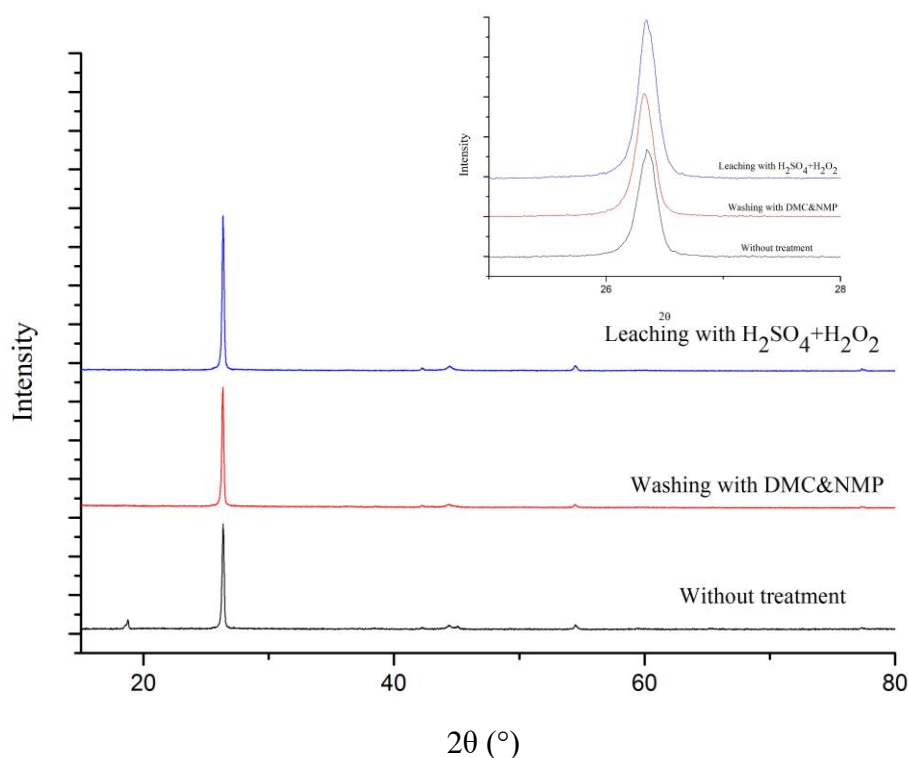


Figure 3. Diffractogram of spent graphite, DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite

The diffractogram indicated that the various forms of intercalation of Li in the graphite (Li_xC₆) and can be identified by the peak characteristics where pure graphite (C) which does not store Li⁺ has a high peak at $26^\circ < 2\theta < 27^\circ$ [20]. As shown in Fig. 2, the strong diffraction intensity of peaks appeared at 2θ of 26.3° according to the characteristic peak of graphite (JCPDS 96-901-2231). This was indicating that the main active material used in the anode of used laptop batteries was accordance with integrated graphite layered structure [21]. Fig. 3 showed that the recycled graphite material has good crystallinity indicated by its sharp peaks. The 2θ peaks of spent graphite, washed graphite, and leached graphite were 26.37° , 26.32° , and 26.33° respectively. All anode materials show differences in their crystallinity. The spent graphite has poorest crystallinity which was indicated by its lowest intensity at 26.37° . In addition, there were weak intensity diffraction peak in the XRD diffractogram at 2θ of 18.70° . This was probably due to the presence of LiMn₂O₄ impurities as predicted by the *Match!* software. The washed graphite showed a higher intensity peak than the spent graphite as seen from its highest intensity at 26.32° . This indicates that the washed graphite has better crystallinity than the spent graphite. The graphite obtained by leaching process has the highest peak intensity at 2θ of 26.3° which means it has the best crystallinity among the three anode materials. The LiMn₂O₄ impurity diffraction peak at 18.70° was no longer appears in the washed graphite and leached graphite diffractograms. This indicates that this treatment has succeeded in removing impurities. Table 2 compares the interlayer distances determined by Bragg's equation as shown in equation 5 [6]:

$$2d \sin\theta = n\lambda \quad (5)$$

The increase in interlayer distance of DMC and NMP washed graphite, and H₂SO₄ + H₂O₂ leached graphite was well established and can be attributed to the co intercalation of solvated Li⁺ during the initial formation of SEI along with the co-insertion of other impurities and decomposed products of electrolyte [6]. According to [15], the expansion of the distance between the graphite layers always results in a high increase in lithium storage capacity. The use of lithium ion batteries was not decompose the anode material structure even though the battery has been damaged and

cannot be used, with the graphite structure on the used LIB anode was not damaged, the graphite in this anode material has the potential to be reused as anode material for new LIB.

Table 2. Physical parameters of spent graphite, DMC and NMP washed graphite, H₂SO₄ and H₂O₂ leached graphite

Sample	2θ (°)	Interlayer Distance (nm)	FWHM
Spent Graphite	26.37	0.337	0.184
Washed Graphite	26.32	0.338	0.167
Leached Graphite	26.33	0.338	0.167

3.4. SEM Images of Anode Active Materials

Wang et al., demonstrated the large particle size in the spent graphite due to the presence of a conductive binder, acetylene black, and electrolyte decomposition products [6]. Fig. 4 show the scanning electron microscope (SEM) images of washed graphite and leached graphite. It can be seen that both anodes show similar morphology. Both graphites show irregular particles with size varying in from 10 to 30 μm and unified morphology of pebbles. There were many small gaps or pores on the particles in leached graphite. In addition, at the edges of the leached graphite there were also exfoliated graphite flakes. The gaps and flakes of exfoliated graphite can shorten the migration distance of Li to the inner surface of the graphite thereby aiding the reaction kinetics and increasing the infiltration between the electrolyte and the electrode [6].

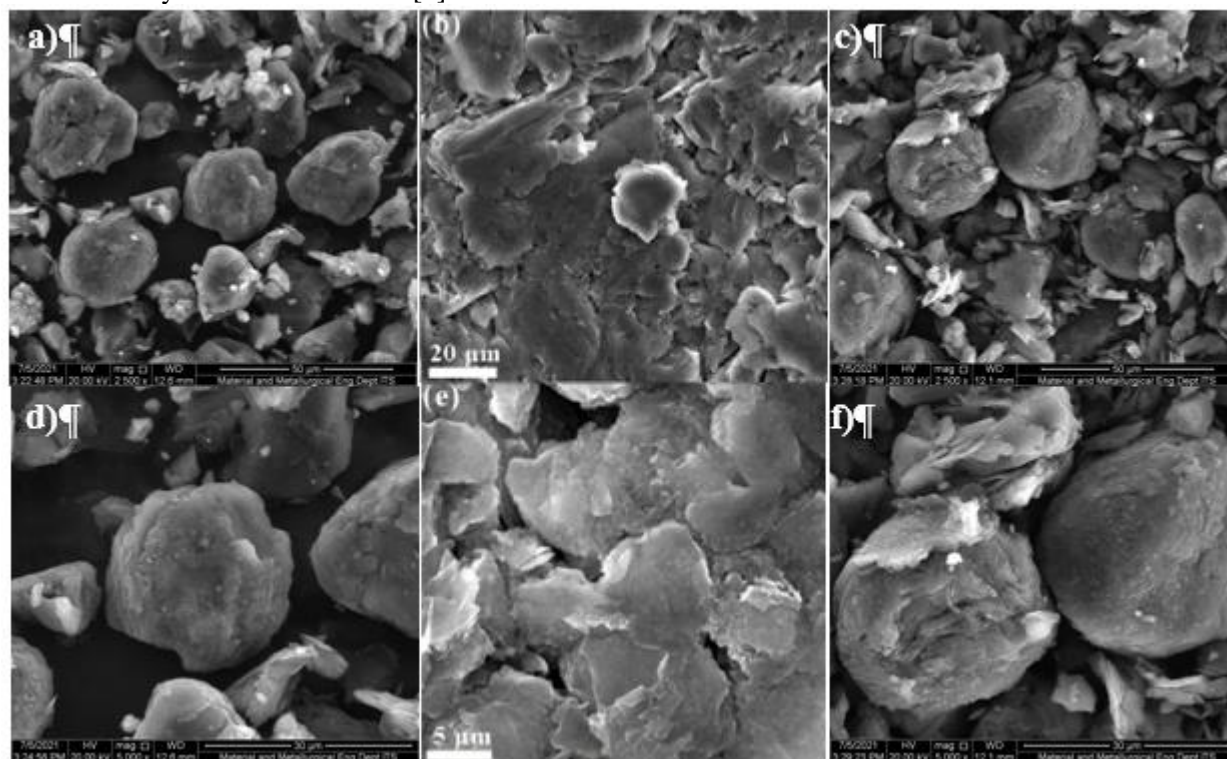


Figure 4. SEM Images of DMC and NMP washed graphite (a&d), spent graphite (b&e) [6], and H₂SO₄ and H₂O₂ leached graphite (c&f)

4. Conclusion

The process was carried out to recover graphite comprehensively, which is important in the sustainable development of LIB. The anode material recycled from used Li-ion batteries was a mixture of graphite, acetylene black, and a

binder. The anode material from recycled LIB was successfully obtained through mechanical separation, washing with organic solvents, leaching process, and heat treatment. Thus, the sulfuric acid leaching process can successfully separate the valuable elements and release the lithium. Graphite in this anode material has the potential to be reused as anode material for new LIB.

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