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Characterization of Copper Oxide (CuO) from Recovery of Cu-Foil Waste by Hydrometallurgical Methods: Acid Leaching and Precipitation

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ABSTRACT: Environmental concerns are increasing due to the rising output of electronic trash (also known as "e-waste"). Lithium-ion batteries, which are commonly used in electronic equipment as high-density energy storage, are one of the sources of e-waste. Due to the abundance of metal resources and potential environmental hazards, recycling lithium-ion battery trash has drawn a lot of interest. Recovery of valuable metals contained in lithium-ion batteries, such as Cu-foil, is one of the efforts to overcome environmental pollution due to copper metal. The hydrometallurgical method is used in the recovery process, which includes leaching using nitric acid and precipitation using oxalic acid. The material obtained was copper oxide (CuO), which was analyzed using XRD, SEM-EDX, and FTIR to determine the characteristics of the sample. XRD analysis showed that the crystallinity of CuO was by the database. SEM images confirm the presence of agglomeration and inhomogeneous particle distribution in the samples. FTIR analysis confirmed the formation of the CuO phase, and the EDX results showed the sample's purity, consisting of Cu and O elements. Based on the research, CuO was successfully produced from the recovery of Cu-foil waste.

Keywords: Cu-foil, Leaching, and Copper Oxide (CuO)

1. Introduction

Due to ever-increasing consumption and rapid technical innovation, many electronic products will eventually become e-waste [1]. E-waste is growing rapidly in the modern era with global volume increasing annually by 3-5% [2]. This increase in the amount of e-waste is a common situation since the 2000s [3]. According to data, e-waste production surged from 33.8 million tons in 2010 to 53.6 million tons in 2019 and is estimated to reach 74 million tons by 2030 [4].

One of the important components found in electronic products is the battery. The energy storage technology known as lithium-ion batteries (LIBs) is widely utilized in portable electronic devices like cell phones, laptops, and digital cameras, and on a large scale in electric vehicles (Evs) [5]. The largest and most prominent secondary energy storage market is dominated by LIBs due to their high energy density, lengthy store lifetime, wide working temperature range, and low self-discharge rate [6]. The projected global LIBs consumption for electric vehicles is estimated to reach $221 billion from 2015-2024 [7]. Meanwhile, LIBs have a life span of 1-3 years which will contribute greatly to the increasing e-waste problem [8]. Used LIBs usually comprise significant amounts of harmful organic and inorganic heavy metal contaminants, which pose a risk to biota, the environment, and human health [9]. The metal container is a valuable metal that could be recycled and recovered as a secondary resource with significant economic potential.

Copper is one of the valuable metals contained in Cu-foil LIBs due to its unique properties such as excellent ductility and high thermal and electrical conductivity. Such good properties make copper metal, one of the essential metals in the world that is widely used by people. However, Cu metal present as waste from e-waste can be a threat to the environment because it is unstable and some spontaneous chemical reactions easily occur even under environmental conditions [10]. Excessive copper intake in the human body will bring adverse effects on hemoglobin which can cause hemolytic anemia, liver damage, and chronic hepatitis [11]. Therefore, recycling and handling copper metal waste is no less urgent than other metal waste.

The hydrometallurgical process is chosen as an effective method for waste recycling due to its mild reaction, environmental friendliness, and high recovery efficiency [12]. Typical hydrometallurgical processes for LIBs waste usually involve leaching using acids, followed by subsequent purification and recovery steps such as adsorption, solvent extraction, and precipitation [13]. Researchers like Habbache et al., reported the leaching process of copper oxide with several acidic solutions including hydrochloric acid, sulfuric acid, nitric acid, and citric acid as leaching reagents in their work on the widespread use of acidic solutions in the leaching of copper [14]. In this study, nitric acid (HNO_3) is used which is considered to have several advantages in leaching systems such as lower corrosiveness for equipment, fully ionized in liquid media, regenerable, low cost, and high recovery efficiency [15].

The compound to be produced in this study is copper (II) oxide (CuO) which is a well-known p-type semiconductor material with high-temperature superconductivity and huge magnetoresistance [16]. CuO is widely utilized in a variety of industries, including energy storage and conversion through environmental science, electronics, and sensors [17]. CuO is also regarded as a possible alternative anode material because of its high specific capacity of 674 $mAhg^{-1}$, compatibility with the environment, an abundance of global sources, economic accessibility, and simplicity of synthesis [18]. Therefore, obtained CuO material from used Cu-foil waste using a leaching method is the novelty presented in this research. This study aims to raise the standard of materials and discover CuO's potential through the recovery of Cu-foil waste. Also, it can lower production costs while addressing waste accumulation and a shortage of copper metal as a result of rising demand.

2. Experimental Method

2.1 Material

Preparation of CuO materials using several raw materials, such as Cu-foil from used LIBs anodes, nitric acid (HNO_3), water, and oxalic acid ($H_2C_2O_4.2H_2O$). While the equipment used is a digital balance, measuring cup, beaker glass, magnetic stirrer, Erlenmeyer funnel, filter paper, mortar and pestle, porcelain cup, hotplate, and furnace.

2.2 Methodology

2.2.1 Preparation of CuO

CuO materials are produced from leaching, precipitation, and sintering processes. The leaching process begins by immersing the used Cu-foil in a container filled with water to remove the anode layer. Cu-foil that has been cleaned is dried and blended to make it smaller in size. Nitric acid (HNO_3) was employed in this study as leachate to recycle Cu-foil. The leaching experiment was carried out in a 1L beaker on a hotplate, which was used to adjust the temperature and speed of stirring with the magnetic stirrer. The concentration of HNO_3 solution used was 2M at 80°C and 60 minutes [19]. The mass composition of Cu-foil and HNO_3 solution in the leaching process is adjusted according to the stoichiometric ratio between Cu and HNO_3, which is stated as follows:

$$3Cu + 8\,(HNO_3) \rightarrow 3Cu\,(NO_3)_2 + 4H_2O + 2NO$$

Cu-foil which has dissolved into a blue solution is then filtered and precipitated by adding a solution of $H_2C_2O_4$, which is equimolar to Cu. The precipitation process takes place with stirring for 60 minutes plus 30 minutes set aside to stabilize. Filter the precipitation results with filter paper, and the precipitate is dried in an oven. The resulting product is copper oxalate precursor (CuC_2O_4) in powder form which is pulverized with mortar and pestle. The sintering process was carried out in a furnace at 500°C for 4 hours to obtain the active material CuO.

2.2.2 Characterization of materials and electrochemical performance test.

Characteristic testing for CuO materials included morphological observations using the JEOL Benchtop Scanning Electron Microscopy JCM 7000, which has an optimal magnification of up to 20000 x and has an EDX multipoint energy dispersion spectrometer (EDX) to determine the material's atomic build. The sample's crystallinity was evaluated using X-ray Diffraction (XRD) on the MD10 Minidifractometer (MTI), which has an exposure time of 1000 seconds and a theta angle range of 17°-71°. Functional group analysis with Fourier transforms infrared (FTIR) using the Shimadzu IR Spirit instrument, which scans from 400 to 4000 cm^{-1} wavelength.

3. Results and Discussion

CuO sample crystalline phase composition was determined using XRD characterization. The XRD pattern of CuO is shown in Figure 1(a) as a diffractogram graph in the form of an arrangement of lines and peaks with specific positions and intensities.

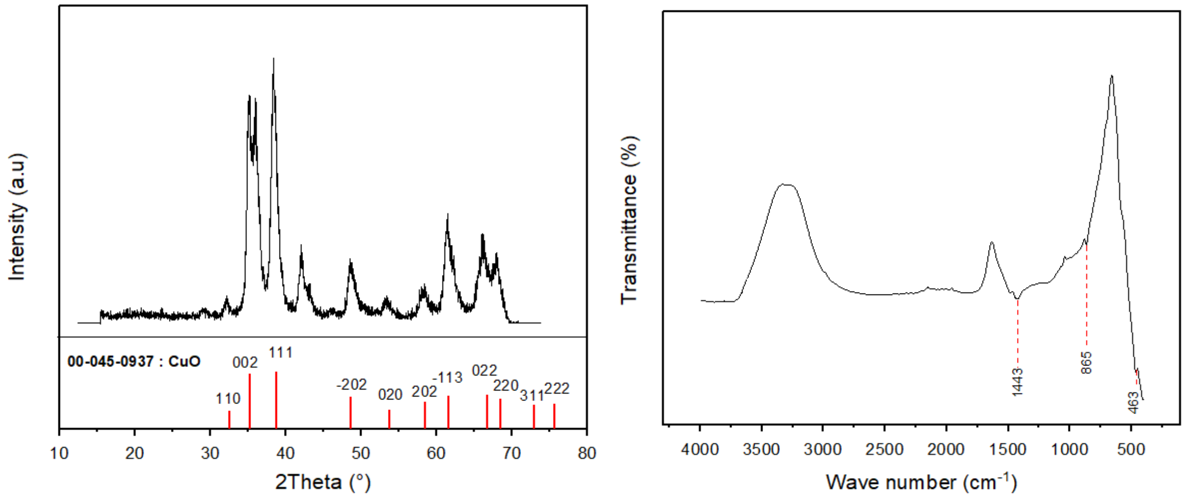

Figure 1. image of (a) XRD pattern and (b) FTIR spectra of CuO

Determination of the suitability of the crystal structure was carried out through qualitative analysis by matching each diffraction peak formed on the JCPDS PDF data: 00-045-0937. The presence of peaks formed from the diffraction data indicates that the CuO sample is crystalline and not amorphous. There are 3 sharp and intense diffraction peaks at positions 35.61°, 38.44°, and 61.59° which show the existence of tenorite (CuO) as a primary component in the monoclinic unit cell will space group C2/c and which correlate to the orientation planes (002), (111), and (113). While the crystal size was calculated using the Scherrer equation, at the highest peak position (111), a crystal size of 9.29 nm was obtained, and the average size of CuO crystals was 9.82 nm. The diffractogram pattern formed from the CuO sample is following the diffraction result of the CuO nano powder produced by Vakylabad et al., through the bioleaching process of chalcopyrite-ore [20].

In addition, there are impurity peaks at positions 36.06° and 42.28°, which can be indexed by Cu_2O based on JCPDS card No. 01-074-1230, in a work by Hajnorouzi et al., copper (II) oxide was created on CuO samples using typical electrochemical procedures before sintering [21]. The appearance of a small amount of cuprite (Cu_2O) in the sintered CuO sample was allegedly caused by partial oxidation due to the presence of a small amount of air and represented separate oxidation particles, as stated by Temujin et al., in the gas evaporation-condensation method for producing copper and silicon/copper powders [22].

The measurement of IR radiation absorption by a material using FTIR spectroscopy and the results are represented in terms of wavelength. The correlation between the sample's chemical composition and the absorption band (vibrational band) is a component of the examination of the IR spectra. Figure 1(b) displays the CuO sample's FTIR spectrum, where there is an absorption peak at a wavelength of 463 cm^{-1}, which indicates stretching of the Cu-O bond vibrations in the CuO monoclinic [23, 24, 25]. In addition, smaller peaks at a wavelength of 865 cm^{-1} can be assigned to the aromatic bending vibration of the C-H group [26]. And the absorption band of 1443 cm^{-1} shows C-O bending vibrations [20].

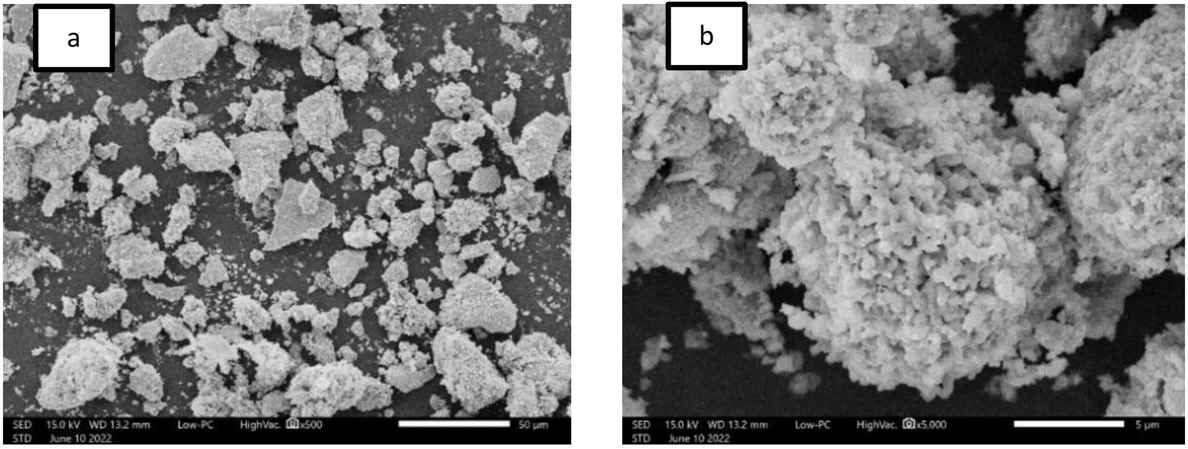

Figure 2. SEM results of CuO at (a) 500x magnification and (b) 5000x magnification

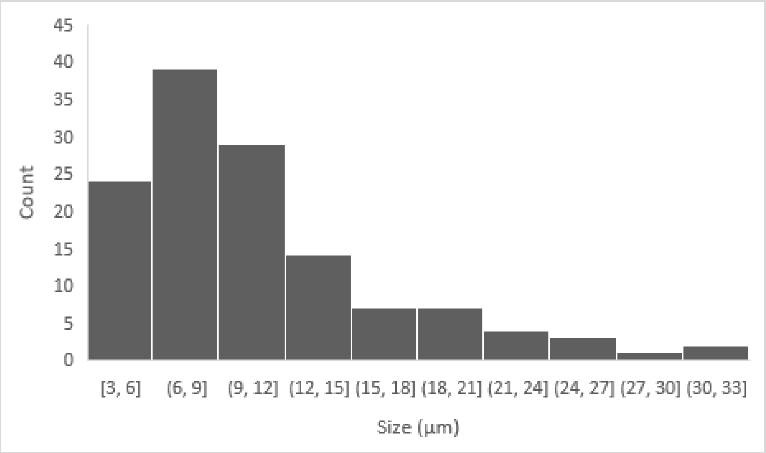

Figure 3. CuO particle size distribution

An observation of the morphology of CuO particles resulting from the leaching of Cu-foil was evaluated using a scanning electron microscope (SEM). SEM characterization provides information regarding the morphology and size of the samples tested. Sampling in SEM was carried out with a magnification of 500 to 5000 times. The morphological results obtained are shown in Figure 2. The 500x magnification in Figure 2(a) shows that CuO samples have a different and non-uniform particle distribution. The distribution of the particles is uneven and shows quite a large scattering with varying sizes, and there is agglomeration. The SEM test on CuO samples obtained sizes within the micrometer range and an inhomogeneous structure.

The distribution of CuO particles is shown in Figure 3, which is the result of measuring the diameter of 130 particles in CuO SEM micrographs. Particle size in microparticle sizes ranges from 3 µm to 33 µm, with an average diameter of 10.34 µm. Only a small number of particles have a large size and the highest frequency ranges from 6 µm – 9 µm. The results obtained are nearly identical to those reported by Zhou et al., who found that the surface of the Cu block obtained has a rough structure consisting of large accumulations ranging in size from 5 µm to 15 µm [27].

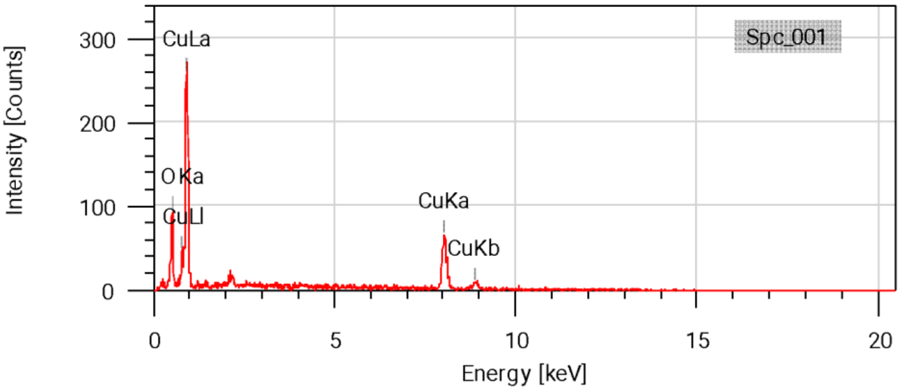

Figure 4. EDX spectra of CuO

Table 1. Elemental mass percentage of CuO from EDX analysis

Element	Mass%	Atom%
O	14.58±1.53	40.40±4.24
Cu	85.42±9.09	59.60±6.34
Total	100.00	100.00

EDX spectra were used to confirm the element composition of CuO, and figure 4. illustrates this. Five elemental peaks have been detected in the host material CuO; four for copper element ($L1, L\alpha, K\alpha$, and $K\beta$) located at binding energies of 8.03, 8.9, 0.91, and 0.53 keV, respectively, and one for oxygen element ($K\alpha$) located at 0.77 keV. Additionally, the components contained in the sample were also confirmed by the EDX results presented in Table 1. It shows that the CuO sample recovered from Cu-foil only consisted of Cu and O elements with a mass percentage dominated by Cu elements, namely 85.42%, and a mass percentage for O elements of 14.58%. As for the percentage of atoms, it shows almost the same ratio between Cu and O elements, namely 59.60% and 40.40%. No impurities were found in the CuO sample, which confirmed the purity of the material.

4. Conclusion

CuO material was successfully obtained from the Cu-foil recovery process using the leaching method with nitric acid, as shown in the results of the characterization test. The resulting XRD peaks match the JCPDS data on CuO with a monoclinic crystal structure and a crystal size of 9.82 nm. SEM and EDX morphology tests showed agglomeration and uneven distribution with an average particle size of 10.34 μm. as well as the FTIR test confirmed the presence of Cu-O bonds in monoclinic CuO.

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Author Contributions

The authors confirm the paper as follows: Wiwin Dwiana carried out the experiment and wrote the manuscript with the support of Muhammad Nur Ikhsanudin. The Report was revised by Himmah Sekar Eka Ayu Gustiana and Risa Suryana.

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