

Research Article

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Cu-foil modification for anode-free lithium-ion battery from electronic cable waste

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Abstract: Batteries are a very efficient energy source used in an all-digital environment that adapts to today's human mobility. The lithium-ion battery is one of the batteries used in various household appliances. There are some problems caused by the anode in terms of utility. This is due to high electrochemical reactivity, which can reduce battery performance. One of the innovations in lithium-ion batteries is anode-free Li-ion battery (AFLB). The working mechanism of this battery is the same as the previous Li-ion battery, but with a smaller anode capacity, so that it can reduce the volume (large) of the battery. The problem that arises is the growth of dendrites that interferes with the battery's running mechanism, so it needs to be evaluated for its growth. The way that can be done is to modify the copper foil by adding Cu. The innovation of this research is to modify Cu-foil by adding Cu from cable waste. The research method used is leaching Cu from cable waste, followed by reducing Cu powder to form a modified Cu. This study's data collection techniques include empirical

research derived from previous studies and instrumental analysis using SEM, FTIR, and electrochemical performance tests. Electrochemical testing using a cylindrical battery with a current of 1 C ($1\text{ C} = 430\text{ mA g}^{-1}$) and a voltage of 2.6–4.3 V obtained ALFB and ALFB Cu-modification batteries with a discharge capacity of 70 and 123 mA h g^{-1} , respectively.

Keywords: copper foil, anode free, copper, cable waste

1 Introduction

Energy has become one of the important aspects of daily activities. Human mobility currently depends on digital and portable items that can be used using energy. The use of goods such as cellphones, laptops, lights, and electric or hybrid-based vehicles requires an energy source in the form of an electric storage device. Batteries are currently the most efficient energy source for use in the mobility of human life. Currently, batteries with lithium-ion are one of the batteries used, both in households and other appliances. Therefore, the development of Li-ion batteries continues to be carried out to get more efficient, lightweight, not too big, have a good cycle, and high capacity. The development of battery technology can be done through design, characteristics, performance, and costs in development [1].

In Li-ion batteries, there are several problems caused by the anode used in terms of the utility of the anode. High electrochemical reactivity causes several issues, such as electrolyte consumption, continuous corrosion, uncontrolled growth of dendrites, and formation of an irreversible solid electrolyte interface passive layer [2]. There is an innovation in using anode-free Li-ion batteries (AFLBs) to overcome this. The working mechanism of this battery is the same as the previous Li-ion battery, but the anode used is smaller in capacity so that it can reduce the volume (large) of the battery [3]. AFLB has caught great attention for implementation in the development of Li-ion batteries. These batteries have proven significant cost reductions and more straightforward

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manufacturing procedures without anodes. Some researchers, such as Ko [4], have designed the more practical AFLB. Dahn's group [5] developed double-salt electrolytes for high-performance bag cell AFLB. However, there is a problem, namely the uncontrolled growth of dendrites. The growth of dendrites can interfere with the running mechanism of the battery, so it is necessary to evaluate its growth. The way that can be done to overcome this is to modify the copper foil (Cu-foil) in the battery by adding Cu to it. Several researchers have proven that the addition of Cu can improve the battery life cycle and increase the capacity for Li-Ion batteries, one of which is a study conducted by Y. Wang [6]. Y. Wang [6] modified Cu_2O by adding nanoparticles. Cu maximizes the capacity and cycle of the battery. Dendritic growth is the primary failure mechanism when Li metal is used as the anode of rechargeable batteries. Due to the breakdown of the surface film in the Li deposit, the new Li surface will be exposed and react with the electrolyte and form an solid electrolyte interphase (SEI) film. If it continues, it will lower the cycle efficiency and the cycle life. The dendrites formed will shorten the battery and create safety problems [7].

Therefore, the right solution to overcome the problems that have been described, modification of Cu-foil, can be done by adding Cu, thereby reducing dendrites in the battery. Cu is obtained from electronic cable waste. Cables are one of the objects that are widely used in everyday life. Unfortunately, the processing of waste from cables is not done correctly. Based on The Global E-waste Monitor 2017 Quantities, Flows, and Resources calculations, the electronic waste generated by the Indonesian population in 2016 was 1.274 million tons [8]. Electronic waste is included in B3 waste, which is dangerous when not processed. B3 waste from service infrastructure, including electronic waste, in 2017 reached 6.03% [9]. In cable waste, there are dangerous compounds, so if ignored, they can pollute the environment and interfere with human health. Using Cu from cable waste is considered effective in reducing cable waste and improving AFLB so that the development of Li-ion batteries is getting better.

2 Materials and methods

2.1 Materials

The tools used are mortar and pestle, porcelain cup, a bottle of the sample, alumina crucible, cylinder cell, pH indicator, filter paper, power supply, Erlenmeyer, digital scale,

beaker, magnetic stirrer, dropper, thermometer, oven, furnace, Newer battery analyzer, Scanning Electron Microscopy (SEM), Eight-channel battery analyzer, Cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS) battery performance test and application.

Materials used are distilled water, electronic cable waste, commercial NMC cathode, sulfuric acid (H_2SO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), nitric acid (HNO_3), *N*-methyl pyrrolidone (NMP), acetylene Black (AB), polyvinylidene fluoride (PVDF), graphite powder, and electrolyte solution (LiPF_6).

2.2 Methodology

The sequence of making an AFLB was divided into three stages: making Cu from used electronic cable waste, modifying Cu-foil in the manufacture of Anode Free Li-ion Batteries, and testing battery performance. The diagram of the research process is shown in Figures 1 and 2.

2.2.1 Research steps

In the first mixing stage, 5 mL of concentrated H_2SO_4 was added to a beaker glass, then continued with the addition of 20 mL of distilled water while stirring slowly [10]. Then a piece of copper weighing 1.25 g was added to the stirred solution [10]. Then, HNO_3 was added and stirred until the brown gas disappeared. The results of mixing I were filtered.

2.2.2 Making Cu from electronic cable waste

In the second mixing stage, copper sulfate solution (CuSO_4) resulting from leaching solution is precipitated using oxalic acid solution. The CuSO_4 solution is added to oxalic acid solution, as precipitating agent, with a concentration of 1.0 M to form Cu oxalate precipitate [11]. The slurry of Cu oxalate was dried using the oven for 12 h with the temperature of 100°C until the slurry perfectly dried and forms Cu oxalate dried powder.

The result of dried Cu oxalate was reduced by adding graphite powder with a mass ratio of 1:0.1 then sintered in a furnace to a temperature of 800°C with a heating rate of $12^\circ\text{C min}^{-1}$ and isothermal temperature for 30 min to produce Cu powder [12]. Then, the tests were carried out in scanning electron microscope (SEM) and X-ray diffraction (XRD) to characterize the material.

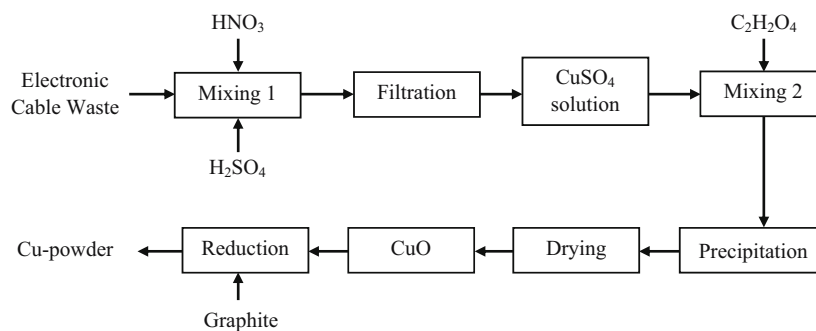


Figure 1: Making Cu powder from electronic cable waste flow chart.

2.2.3 Cu foil modification for AFLB production

Cu powder from electronic cable waste was mixed with PVDF solution and then made a slurry in a mortar. Furthermore, the slurry and Cu-foil were combined through the coating stage to form a layer. Moreover, the coating results in an oven at a temperature of 70°C for 12 h. The commercial NMC cathode material that has been prepared was added with AB and PVDF until everything is homogeneously mixed. Then, NMP is added until it is mixed into a cathode paste. Subsequently, the cathode paste was coated on the aluminum foil sheet using an automatic film coater. The battery film was put in a vacuum oven at 150°C to dry.

The dried battery film and Cu/CuO material are processed to form a cylinder cell battery. The pressing process used a hot rolling machine and molded it into a round shape. Cylinder cells were made by cutting the dried battery film with 10 cm × 5.6 cm as cathode film [13]. While the film material Cu/CuO is cut with 13 cm × 6 cm. After that, the battery component plates are rolled together with the separator based on the separator – modified Cu-foil – separator – cathode arrangement. The cylinder cell battery is placed in a glove box to add an electrolyte solution to the cylinder cell. Furthermore, a Full Cell Test was carried out on the battery using an

eight-channel battery analyzer to determine the performance and capacity of the commercial LNMC battery that had been made.

2.3 Battery performance test

Testing is done using an eight-channel battery analyzer. The data obtained are in the form of specific charge-discharge capacity and efficiency. This test is carried out for 100 cycles with current measurement (*I*) starting from full voltage to empty voltage. The performance test used current rate of 0.1 C with current range of (1–50) mA. The discharge cut of voltage used is 2.5 V, and the charge cut-off voltage is 4.3 V.

3 Result and discussion

3.1 Synthesis of CuSO₄

The process of synthesizing CuSO₄ from electronic cable waste by leaching process using sulfuric acid and nitric acid has been carried out.

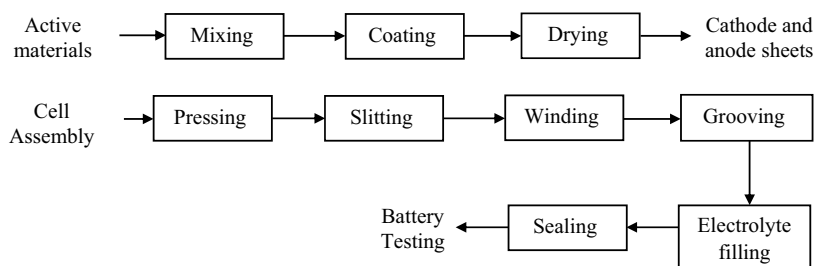


Figure 2: Cu-foil modification for AFLB production flow chart.

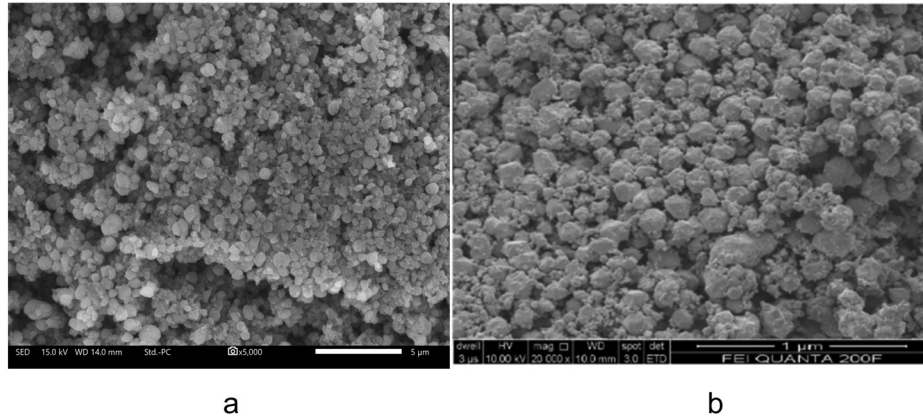
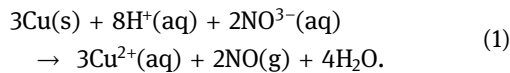
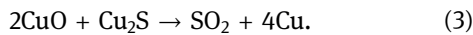
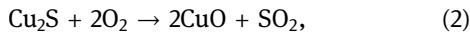


Figure 3: (a) Copper oxalate SEM result (b) copper SEM result [1].

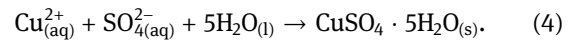
Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), called blue vitriol, is usually used as an electrolytic in copper refining. In electrotyping in some bacteria, printing more or calico stamps as Bordeaux slurry to vanish fungi [2]. One of the properties of copper metal is it is insoluble in non-oxidizing acids, but copper is oxidized by HNO_3 so that copper dissolves in it. The reaction formed is as follows:



Copper metal is made from copper sulfide (Cu_2S) which is oxidized with oxygen:



Copper salts in the solution appeared blue, because they form $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions. If the Cu solution is added to the H_2SO_4 solution, the reaction occurs according to Keenan [12]:



$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can be made using sulfuric acid and nitric acid, which is then heated and concentrated to form a material precursor. In addition, the raw material for copper metal to make $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can also be made from copper waste or sponge copper obtained from CuCl_2 solution. During the heating process of the solution, the increase in reaction temperature increases the solubility of CuSO_4 in water, so more $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are formed.

3.2 SEM-EDX analysis

Copper oxalate produced, and dried, from the leaching and precipitating processes with the addition of oxalate was tested in SEM to determine the type of particles in the sample and their particle size. Figure 3(a) shows the

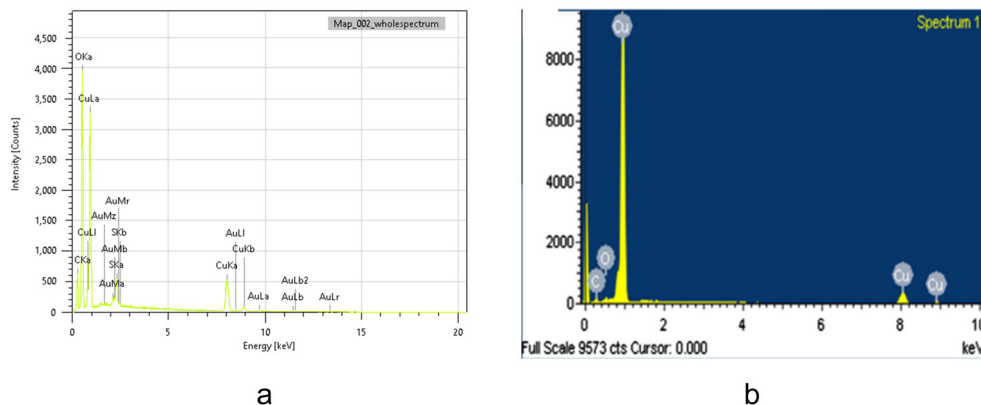


Figure 4: (a) Copper oxalate EDX result. (b) copper EDX result.

morphology analysis of the copper oxalate sample, and Figure 3(b) shows the copper result from the study by Mahadevan and Chauhan [1] for comparison.

The test sample results showed copper oxalate with an average size of 415 nm. The size is in line with the research results conducted in several studies. Mahadevan and Chauhan [1] mentioned that the copper particle size is 70–400 nm with a magnification of 120,000 nm. Rajkumar and Aravindan [14] obtained a copper size of 12 μm or 12,000 nm. Zheng *et al.* [15] mentioned the copper particle size of 10 nm. The process temperature influences the difference in the particle size value, and the resulting stress will also be different. Figure 4 is the SEM-energy dispersive X-ray (EDX) analysis graph due to peaks of each detected component in the sample. Figure 4(a) represents the sample in this research compared to EDX test result obtained from the research by Mahadevan and Chauhan [1].

In the copper results analyzed, the peak of copper oxalate was 8 keV, which was different from the results obtained by Mahadevan and Chauhan [1], in which the value was 8.9 keV. The difference in value is due to the surface size of the analyzed particles. The particle size based on Mahadevan and Chauhan's [1] result has a maximum range

of 400 nm and a voltage of 8.9 keV, while the size of the copper particles tested was 415 nm with a large voltage of 8 keV. The area of copper particles is influenced by the size of the particles, where the larger the particles, the smaller the surface area. The larger the surface area of the analyzed particles, the more extensive the stress testing of the copper particles will be. This allows an increase in the analyzed stress [15]. The difference in the area greatly affects the stress test results, as shown in the graph. The size of 415 nm with a magnification of 20,000 is considered to meet the particle size of copper. The resulting voltage value exceeds the results of previous studies, which can be concluded that copper can be used as an AFLB modification material.

4 XRD Cu powder

The XRD test for CuO precursor was carried out to determine whether the precursor compound formed was appropriate or not, informing the desired CuO precursor.

Figure 5 shows that XRD patterns of CuO already have the exact peak conformity as JCPDS (Joint Committee on Powder Diffraction Standard) Number 05-0661 to assure the material quality. It shows that the precursor compound CuO has been successfully synthesized with a spherical-shaped crystal structure. The XRD pattern formed shows the same pattern as the XRD pattern in the research of Luna *et al.* [16] researched the ratio of the two common forms of CuO crystals formed is α -CuO and β -CuO. As a result, the CuO-NPS sample created has the same structure as β -CuO XRD patterns. After the linear regression calculation, the obtained values are $a = 0.466789 \text{ \AA}$, $c = 0.511844 \text{ \AA}$, and the lattice parameter (c/a) of 1.096521126 $\text{\AA}$ [16], this result is close to the tested sample, which has the value of $a = 4.048969649 \text{ \AA}$, $c = 4.640517204 \text{ \AA}$, and the lattice parameter of 1.146098293 $\text{\AA}$. It shows that the layered structure material formed from the sample is entirely appropriate and systematic.

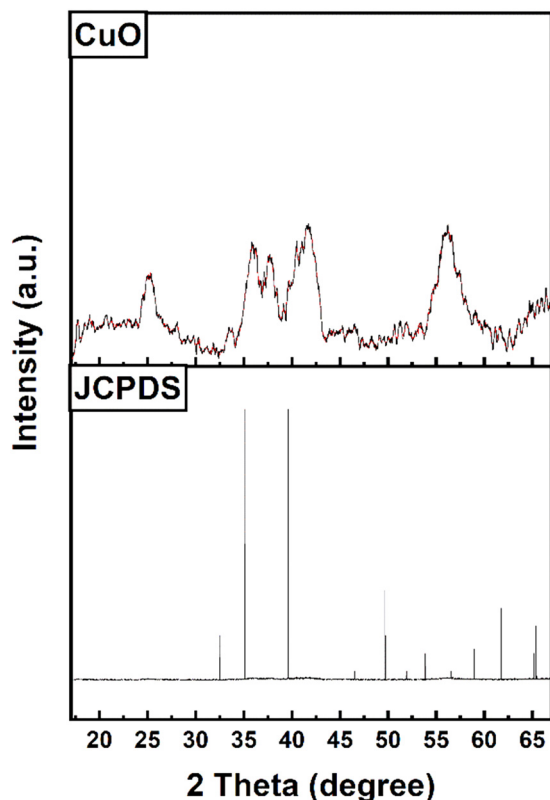


Figure 5: Comparison of XRD Patterns of CuO sample and 05-0661 JCPDS XRD β -CuO-NPS Reference Standard [16].

5 Battery performance analysis

The performance of the AFLB with modified Cu-foil is analyzed using eight-channel Neware Battery Analyzer. The results of this test are specific capacity and cycles performance. The test was based on two samples. First, AFLB with bare Cu-foil (without any treatment or modification), and second, AFLB with Cu-modification. The collecting

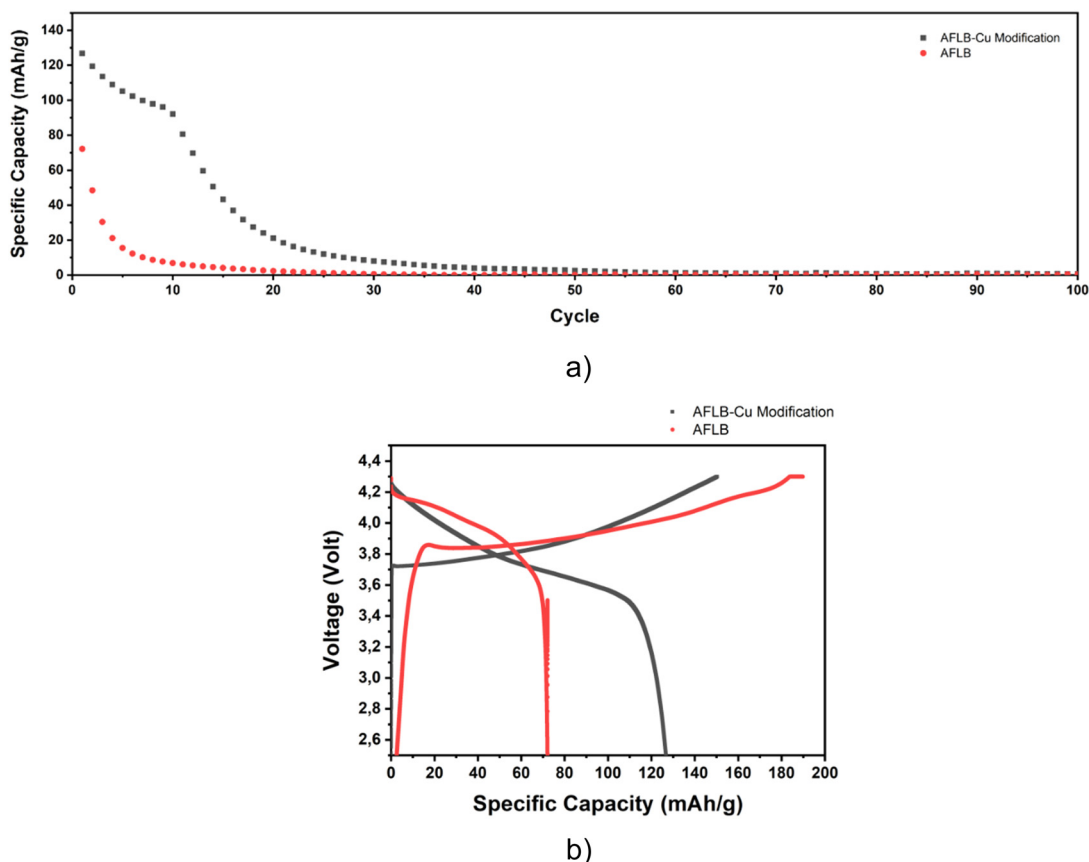


Figure 6: (a) Cyclic performance of AFLB with bare and modified Cu-foil. (b) Initial discharge capacity performance of AFLB with bare and modified Cu-foil.

data were processed in graph formation using Origin software. The graph is obtained is shown in Figure 6.

Figure 6(a) shows cycles performance data, and Figure 6(b) shows specific capacity data of AFLB performance test. The black curves of Figure 6(a) and (b) define battery with modified Cu-foil and the red ones define battery with bare Cu-foil. Figure 6(a) shows the cycle performance of two samples. Based on the test, AFLB with modified Cu-foil showed better cycle performance with better cycle ability on first cycle until 50th cycle. Battery with bare Cu-foil drops at 25th cycles and battery with modified Cu-foil did not drop until 50th cycle. From this result, the cycle performance increased two times with Cu-foil modification as an anode electrode, and the stability showed better performance at the first until 10th cycles. Compared to bare Cu-foil, the capacity drops rapidly at the same initial range of cycles. Figure 6(b) describes the charging and discharging curve for bare Cu-foil and modified Cu-foil AFLBs. The result shows that the discharge capacity of modified Cu-foil is better than bare Cu-foil. The initial discharge capacity increased from 71 to 123 mA h g⁻¹.

6 Conclusion

Using the leaching method, the synthesis of Cu powder from electronic cable waste was successfully synthesized. Technological parameters such as particle surface area affect the difference in stress values in copper oxalate precursors. The resulting voltage value exceeds the results of previous studies, which can be concluded that copper can be used as an AFLB modification material. The XRD patterns of all samples were similar and well-indexed to JCPDS 05-0661 standard. In the electrochemical test of the battery, it was found that the AFLB and Cu-modified AFLB (Cu/Cu oxalate@graphite) at discharge were 100 cycles with the best capacity of Cu-modified AFLB, i.e., 123 mA h g⁻¹.

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Conflict of interest: There are no conflicts of interest to declare.

Data availability statement: The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

References

- [1] Mahadevan S, Chauhan APS. Investigation of synthesized nanosized copper by polyol technique with graphite powder. *Adv Powder Technol.* 2016;27(4):1852–6. doi: 10.1016/j.appt.2016.03.011.
- [2] Fitrony, Fauzi, R, Qadariyah L, Mahfud M. Pembuatan kristal tembaga sulfat pentahidrat (CuSO₄·5H₂O) dari Tembaga Bekas Kumparan. *J Tek Pomits.* 2013;2(1):2–6. <http://ejurnal.its.ac.id/index.php/teknik/article/view/2349%0Ahttps://ejurnal.its.ac.id>.
- [3] Purwanto A, Yudha CS, Ubaidillah U, Widiyandari H, Ogi T, Haerudin H. NCA cathode material: Synthesis methods and performance enhancement efforts. *Mater Res Express.* 2018;5(12):122001. doi: 10.1088/2053-1591/aae167.
- [4] Ho K. Modelling of charge/discharge cycle of the lithium-ion battery system. *J Qual Meas Anal.* 2014;10(1):39–47.
- [5] Genovese M, Louli AJ, Weber R, Hames S, Dahn JR. Measuring the Coulombic efficiency of lithium metal cycling in anode-free lithium metal batteries. *J Electrochem Soc.* 2018;165(14):A3321–5.
- [6] Wang Y, Cao L, Li J, Kou L, Huang J, Feng Y, et al. Cu/Cu₂O@Ppy nanowires as a long-life and high-capacity anode for lithium-ion battery. *Chem Eng J.* 2020;391(August):123597. doi: 10.1016/j.cej.2019.123597.
- [7] Wahyono S. Kebijakan Pengelolaan Limbah Elektronik Dalam Lingkup Global Dan Lokal = Electronic waste management policies in the scope of global and local. *J Teknol Lingkung.* 2016;14(1):49.
- [8] Balde CP, Forti V, Gray V, Kuehr R, Stegmann P. The global e-waste monitor 2017. United Nations University; 2017. p. 1–116. http://collections.unu.edu/eserv/UNU:6341/Global-E-waste_Monitor_2017__electronic_single_pages_.pdf.
- [9] Rositawati A, Taslim C, Soetrisnanto D. Rekrystalisasi garam rakyat dari daerah demak untuk mencapai sni garam industri. *Teknol Kim dan Ind.* 2013;2(4):217–25.
- [10] Rodiah S, Widya Budaya A, Erviana D, Ahsanunnisa R, Oktasari A, Wijayanti F, et al. Pembuatan kristal tembaga(ii) sulfat pentahidrat dengan variasi ukuran tembaga bekas. *Pros Semin Nas Sains dan Teknol Ter.* 2018;1(1):167–71.
- [11] Jia Z, Yue L, Zheng Y, Xu Z. The convenient preparation of porous CuO via copper oxalate precursor. *Mater Res Bull.* 2008;43(8–9):2434–40.
- [12] Purwanto A, Yudha CS, Ubaidillah U, Widiyandari H, Ogi T. NCA cathode material: synthesis methods and performance enhancement efforts NCA cathode material: synthesis methods and performance enhancement efforts. *Mater Res Express.* 2018;5(12):122001.
- [13] Thowil Afif M, Ayu Putri Pratiwi I. Analisis Perbandingan baterai lithium-ion, lithium-polymer, lead acid dan nickel-metal hydride pada penggunaan mobil listrik – review. *J Rekayasa Mesin.* 2015;6(2):95–9.
- [14] Rajkumar K, Aravindan S. Microwave sintering of copper-graphite composites. *J Mater Process Technol.* 2009;209(15–16):5601–5.
- [15] Zhang X, Zhang D, Ni X, Zheng H. Optical and electrochemical properties of nanosized CuO via thermal decomposition of copper oxalate. *Solid-State Electron.* 2008;52(2):245–8.
- [16] Luna IZ, Hilary LN, Chowdhury AMS, Gafur MA, Khan N, Khan RA. Preparation and characterization of copper oxide nanoparticles synthesized via chemical precipitation method. *OALib.* 2015;02(03):1–8.