Journal of Social Research

P-ISSN: 2827-9832
E-ISSN: 2828-335x
http://ijsr.internationaljournallabs.com/index.php/ijsr

EFFECT OF MILLING TIME AND ADDITION OF GRAPHITE ON THE MORPHOLOGICAL STRUCTURE OF TIN PHOSPHATE POWDER USING THE GRAPHINE OXIDE TEMPLATE METHOD FOR ELECTROLYTE APPLICATIONS

Joseph Bona Nandito[1*], Calvin Santo Arnoldus[2], Bachtiar Zuhdi Alfarizi[3***], Bismo Aditiya Prakoso[4****], Adhitya Trenggono[5*****]**
[1,2,3,4,5]*Universitas Sultan Ageng Tirtayasa*
[*] josephbona30@gmail.com [**] carnoldus48@gmail.com [***] bachtiaralfarizi@gmail.com
[****] bismoap@gmail.com [*****] metalurgi@untirta.ac.id

ABSTRACT

Tin phosphate can be used for electrolyte applications. The solid electrolyte industry has experienced significant growth in recent years. In 2020, the market size of the solid electrolyte industry was estimated at $17.8 million and is expected to reach $56.6 million by 2030 at a CAGR of 12.1% from 2021 to 2030. The growth of the solid electrolyte industry is driven by the increasing demand for batteries. Solid-state batteries are becoming a promising alternative to conventional lithium-ion batteries. This research produces tin phosphate nanoparticles through the synthesis of tin phosphate/GO with a modification of the Hummers reaction, using the GO template method which is used to control the morphology and crystal structure of the synthesized material, and calcined to remove GO and produce tin phosphate powder. The research results show that graphite milling time influences the size of the tin phosphate powder produced, and the size of the Graphene Oxide (GO) template also influences the size of the tin phosphate powder. Grinding time also affects the weight of the powder before and after calcination, as well as the amount of GO and tin phosphate produced. The graphite addition ratio also had a significant effect on the weight of the tin phosphate/GO samples before and after calcination. The ratio of adding 2 grams of graphite to 1 gram of tin produces an optimal weight of tin phosphate after calcination, indicating the effectiveness of using GO as a tin growth template. In addition, XRD analysis showed the identification of three dominant compound phases in the resulting powder, namely potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$), tin phosphate (SnP_2O_7), and potassium ferrate ($FeKO_2$).

Keywords: *Tin Phosphate, Solid State, Electrolyte, Graphene Oxide, Template Method*

INTRODUCTION

Indonesia has quite abundant tin reserves. These reserves are found in many plains and along the Bangka, Belitung, Kundur, and Singkep islands (Suharyanto & Hanum Lalasari, 2016). The potential for tin minerals in Indonesia is quite large, but it has not yet been exploited optimally (Surya & Yusuf, 2020). Indonesia is the second largest tin-producing country after China with an annual production of 84,000 tons (Suprapto, 2008). One of the areas known as a tin (Sn) producer in Indonesia is the Bangka Belitung Islands. The reserves are spread quite widely, over 800 kilometers known as The Indonesian Tin Belt (Catur et al., 2015). Increasing world consumption has resulted in less demand for tin being met. If this need is met by exploration, environmental damage will occur. Efforts that can be made include looking for other alternatives that replace the role of tin or changing tin into new compounds that have higher economic value, for example, tin dioxide as a catalyst. In this way, tin optimization efforts from upstream to downstream are prospectively carried out. Tin can be used as an electronic component, brake lining, electrode, infrared ray reflector, gas detector, and chemical reaction catalyst (Prodjosantoso et al., 2011). These tin applications are usually used in the form of nanoparticles, such as nanosheets, nanorods clusters, nanopyramids and nanoplates, nanorod arrays, nanorod bundles, and nanospheres (Shaalan et al., 2016). Tin phosphate can be used for electrolyte applications. The solid electrolyte industry has experienced significant growth in recent years. In 2020, the market size of the solid electrolyte industry was estimated at $17.8 million and is expected to reach $56.6 million by 2030 at a CAGR of 12.1% from 2021 to 2030. The growth of the solid electrolyte industry is driven by the increasing demand for batteries. Solid-state batteries are a promising alternative to conventional lithium-ion batteries (Snehal and Eswara, 2021). The nano-sized tin powder has been produced by various methods. The methods usually used are hydrothermal, polymers, organo-metal precursor synthesis, sonication, microwave, and surfactant-mediated methods (Bhagwat et al., 2015). Synthesis using templates is the most promising approach because it can control the shape and size of nanowires by changing the pores in the template (Meng et al., 2020a). Therefore, milling the template can affect the size of the resulting powder. The template used is graphene oxide using waste graphite from steel smelting electrodes using an electric arc furnace (EAF). Previous research carried out tin synthesis by modifying the Hummers method using 3 grams of graphite (passing a 500 mesh sieve) and 100% DMF dispersion solvent media to produce tin phosphate with a smaller and more spherical size and with a 2θ value of 31.7242 and d hkl 2 .81824 Å (Ardhi, 2022). Previous research on the synthesis of Sn/GO was carried out by hydrothermal assembly using a graphene oxide template. The results of the graphene oxide template analysis can distribute tin dioxide with a size of 2 to 100 nanometers with a macro pore size of 3 to 10 microns and a pore volume of 0.321 cm3.g-1 and a surface area of 237.7 cm2.g-1 with a homogeneous distribution of SnO (Pei et al., 2015). To get tin dioxide that is close to a spherical shape, it is necessary to wrap the graphene membrane. In previous research, the morphological transition from graphene oxide nanomembranes to nanoscrolls was possible using dimethylformamide in the DMF dispersion. because the Dimethylformamide content ranges from 30% by volume to 100% by volume, it can roll up Graphene Oxide and form nanoscrolls in low concentrations of Graphene Oxide (<0.05 mg/mL) (Tang et al., 2018). This research synthesizes tin in a Hummer's reaction with GO as a tin growth template. Graphene oxide will later be calcined so that tin phosphate powder remains.

METHOD

Electric arc furnace or EAF graphite electrodes measuring 50 cm in diameter, and 80 cm high are reduced to a size of -400+500 mesh using a ball mill machine. Then it was milled again using a Planetary Ball Mill, graphite -400+500 mesh was put into two 500 mL jars, each jar was filled with 25.3 grams of graphite then milled with BPR (Ball to Powder Ratio) 10:1, milling speed 300 rpm and with three milling time variations of 5 hours, 10 hours and 15 hours using the dry milling method, 50 grams were obtained from each time variation, and it was ready to be synthesized into graphene oxide using the modified Hummers method. The process of making tin phosphate with a graphene oxide (GO) template is carried out by weighing 1 gram of tin and dissolving it with H_2SO_4 solution at a temperature of 180°C in a beaker for 45 minutes. Next, weigh the graphite with variations of 1 gram (B1), 2 grams (B2), and 3 grams (B3) with milling time variations of 5 hours (M1), 10 hours (M2), and 15 hours (M3) respectively put in a beaker. 13.3 mL H_3PO_4 solution was added to a beaker which was maintained at a temperature of 97°C and stirred for 1.5 hours. Next, the mixture was cooled to room temperature. After cooling, 15 grams of $KMnO_4$ was added slowly and continued with stirring for 30 minutes in an ice bath.

Next, the mixture was stirred at a temperature of 40°C for 30 minutes. The mixture is allowed to cool until the color changes to green. After the mixture changed color, 250 mL of distilled water and 20 mL of H_2O_2 were added and stirred slowly for 30 minutes. Next, after leaving it overnight, the mixture was dispersed with liquid hydrogen chloride and then washed repeatedly seven times with distilled water. Then the mixture is tested with blue litmus paper to universal pH paper. If it shows a paper color that is close to neutral, it is filtered to get sediment and dried in an oven. The process of making tin phosphate by calcining powder to decompose graphene oxide (GO) in a furnace at a temperature of 900°C for 6 hours. SEM testing was carried out to determine the morphology of the powder before calcination and the powder after calcination obtained, what shape the tin phosphate produced using the GO template and to determine whether the surface shape of the particles was rough or smooth. X-ray diffraction (XRD) testing was carried out to determine the characterization of tin dioxide to confirm the chemical compounds and crystal structures formed. The results of the XRD testing were then analyzed using the high score plus (HSP) application. The XRD results file is opened in the HSP application, then the background on the XRD graph, and then search for peaks, and fit the profile. After that, search and match is carried out by adjusting what elements are in the powder. Then the compounds that may be present in the powder will appear and look for which compounds whose peaks match the XRD graph of the resulting powder. Particle size analyzer (PSA) characterization aims to determine the average specific size of powder material such as volume diameter, particle size, and particle size distribution values. PSA characterization in this study was carried out by dispersing powder weighing 0.001 grams with 10 mL of ethanol in a sonication apparatus for 15 minutes. After that, just take a small amount using a pipette, then put it into a cuvette. The cuvette containing the dissolved powder is then inserted into the PSA test equipment for subsequent characterization.

RESULTS AND DISCUSSION

Table 1. Sample Equations

Sample Name	Graphite Milling Time	Graphite Addition
M_1B_1	5 Hours	1 gram
M_1B_2	5 Hours	2 grams
M_1B_3	5 Hours	3 grams
M_2B_1	10 Hours	1 gram
M_2B_2	10 Hours	2 grams
M_2B_3	10 Hours	3 grams
M_3B_1	15 Hours	1 gram
M_3B_2	15 Hours	2 grams
M_3B_3	15 Hours	3 grams

Table 1 shows the variations in graphite milling time used and the addition of graphite. The Hummers modification method was carried out to synthesize Sn/GO to obtain tin dioxide nanoparticle powder. This method uses 1 gram of tin with a content of 99.9%, H_2SO_4, 1, 2, and 3 grams of graphite which has previously been milled with varying graphite milling times of 5, 10, and 15 hours, added to the H_3PO_4 solution, then an oxidizer is added. $KMnO_4$ for 3 hours synthesis time. Next, calcination is carried out to obtain tin dioxide powder.

Based on the graphite milling time which was varied into 3, namely, 5 hours, 10 hours, and 15 hours, to obtain the specific particle size it was analyzed using a particle size analyzer (PSA), with the size distribution of each initial characterization sample of graphite milling and the final sample Tin phosphate is analyzed in Table 2.

Table 2. PSA (Particle Size Analyzer) Results Particle Size Distribution

PSA Early Graphite		
Sample Name	**Z-Average (nm)**	**Polydispersity Index value (PI)**
M_0	3681	1
M_1	3381	1
M_2	2414	1
M_3	2830	0,9359
PSA Final Tin Phosphate		
M_1B_1	1317	0,3812
M_1B_2	1127	0,3632
M_1B_3	1144	0,4764
M_2B_1	582,3	0,7045
M_2B_2	355	0,3599
M_2B_3	693,1	0,1571
M_3B_1	752,9	0,5281
M_3B_2	841,9	0,6626
M_3B_3	847,8	0,5731

After the synthesis and calcination process, tin phosphate powder is obtained. Tin phosphate powder was characterized using a particle size analyzer (PSA). From Table 2 it can be seen that in the M1B1 sample, the z-average is 1317 nm with a PI value of 0.3812, in the M1B2 sample the z-average is 1127 nm with a PI value of 0.3632, in the M1B3 sample the z-average is 1144 nm with PI value is 0.4764, in sample M2B1 the z-average is 582.3 nm with a PI value of 0.7045, in sample M2B2 the z-average is 355 nm with a PI value of 0.3599, in sample M2B3 the z-average 693.1 nm with a PI value of 0.1571, in the M3B1 sample the z-average is 752.9 nm with a PI value of 0.5281, in the M3B2 sample the z-average is 841.9 nm with a PI value of 0.6626, and on the M3B3 sample the z-average is 847.8 nm with a PI value of 0.5731. The samples that have been synthesized are expected to become tin phosphate/GO material. Before being calcined in the furnace, the samples were weighed first and samples M1B1, M2B1, and M3B1 were found to weigh 1.83 grams, 1.14 grams, and 1, respectively. 61 grams. For samples M1B2, M2B2, and M3B2, the weights were 3.8 grams, 4.41 grams, and 5.6 grams, respectively. And for samples M1B3, M2B3, and M3B3, the weights were 5.45 grams, 7.3 grams, and 7.82 grams, respectively. After that, the sample is calcined in the furnace, it is hoped that it will become tin phosphate material. The final weight of the calcined samples for samples

M1B1, M2B1, and M3B1 was found to be 0.14 grams, 0.2 grams, and 0.47 grams, respectively. For samples M1B2, M2B2, and M3B2, the weights were 1.1 grams, 1.16 grams, and 1.3 grams, respectively. And for samples M1B3, M2B3, and M3B3, the weights were 1.03 grams, 1.13 grams, and 1.45 grams, respectively. Sample weight data can be seen in Table 3.

Table 3. Weight Before Calcination of Tin Phosphate/GO, After Calcination, and West Difference

Before Calcination	
Sample	**Weight of Tin Phosphate/GO (Gram)**
M_1B_1	1,83
M_2B_1	1,14
M_3B_1	1,61
M_1B_2	3,8
M_2B_2	4,41
M_3B_2	5,6
M_1B_3	5,45
M_2B_3	7,3
M_3B_3	7,82
After Calcination	
Sample	**Weight of Tin Phosphate (Gram)**
M_1B_1	0,14
M_2B_1	0,2
M_3B_1	0,47
M_1B_2	1,1
M_2B_2	1,16
M_3B_2	1,3
M_1B_3	1,03
M_2B_3	1,13
M_3B_3	1,45
Weight Difference Before (Tin Phosphate/GO) and After Calcination (Tin Phosphate)	
Sample	**∆Weight (Grams)**
M_1B_1	1,69
M_2B_1	0,94
M_3B_1	1,14
M_1B_2	2,7
M_2B_2	3,25
M_3B_2	4,3
M_1B_3	4,42
M_2B_3	6,17
M_3B_3	6,37

From Table 3 you can also see the difference in sample weight before calcination (tin phosphate/GO) and after calcination (tin phosphate). From this data, it can be seen that the difference in weight for the M1B1 sample is 1.69 grams. In sample M2B1 it is 0.94 grams. In sample M3B1 it is 1.14 grams. Then in the M1B2 sample, it was 2.7 grams. In the M2B2 sample, it is 3.25 grams. In the M3B2 sample, it was 4.3 grams. Furthermore, the M1B3 sample was 4.3 grams. In the M2B3 sample, it is 6.17 grams. And in the M3B3 sample, it was 6.37 grams.

From the results of the X-ray diffraction (XRD) test, it was found that 3 dominant compound phases were present in the resulting powder. The compounds produced are potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$), tin phosphate (SnP_2O_7), and potassium ferrate ($FeKO_2$). From the results of X-ray diffraction (XRD), the crystal size of the compound can also be calculated using the Scherrer equation. Table 4 shows the crystal size and crystal structure of each sample.

Table 4. Crystal Size and Crystal Structure

Sample	Compound	Crystal Size (nm)	Crystal Structure
M_1B_1	$KO_{12}P_3Sn_2$ (98-026-1893)	39,57	Hexagonal
	SnP_2O_7 (00-029-1352)	49,29	Cubic
	$FeKO_2$ (98-015-7785)	50,27	Orthorhombic
M_1B_2	$KO_{12}P_3Sn_2$ (98-026-1893)	29,88	Hexagonal
	SnP_2O_7 (00-029-1352)	51,78	Cubic
	$FeKO_2$ (98-015-7785)	52,83	Orthorhombic
M_1B_3	$KO_{12}P_3Sn_2$ (98-026-1893)	35,28	Hexagonal
	SnP_2O_7 (00-029-1352)	58,87	Cubic
	$FeKO_2$ (98-015-7785)	60,06	Orthorhombic
M_2B_1	$KO_{12}P_3Sn_2$ (98-026-1893)	7,70	Hexagonal
	SnP_2O_7 (00-029-1352)	6,92	Cubic
	$FeKO_2$ (98-015-7785)	119,16	Orthorhombic
M_2B_2	$KO_{12}P_3Sn_2$ (98-026-1893)	32,02	Hexagonal
	SnP_2O_7 (00-029-1352)	68,02	Cubic
	$FeKO_2$ (98-015-7785)	69,39	Orthorhombic
M_2B_3	$KO_{12}P_3Sn_2$ (98-026-1893)	53,57	Hexagonal
	SnP_2O_7 (00-029-1352)	88,57	Cubic
	$FeKO_2$ (98-015-7785)	90,35	Orthorhombic
M_3B_1	$KO_{12}P_3Sn_2$ (98-026-1893)	40,17	Hexagonal
	SnP_2O_7 (00-029-1352)	86,31	Cubic
	$FeKO_2$ (98-015-7785)	88,04	Orthorhombic

Sample	**Compound**	**Crystal Size (nm)**	**Crystal Structure**
M_3B_2	$KO_{12}P_3Sn_2$ (98-026-1893)	34,68	Hexagonal
	SnP_2O_7 (00-029-1352)	74,74	Cubic
	$FeKO_2$ (98-015-7785)	76,24	Orthorhombic
M_3B_3	$KO_{12}P_3Sn_2$ (98-026-1893)	31,65	Hexagonal
	SnP_2O_7 (00-029-1352)	32,93	Cubic
	$FeKO_2$ (98-015-7785)	57,95	Orthorhombic

Figures 2 to 4 show the SEM-EDS results of powder before and after calcination on the M3¬B3 sample. It can be seen that the powder before calcination still shows layers, whereas the powder after calcination does not show a layer, which indicates the loss of GO as a template after calcination at a temperature of 900°C.

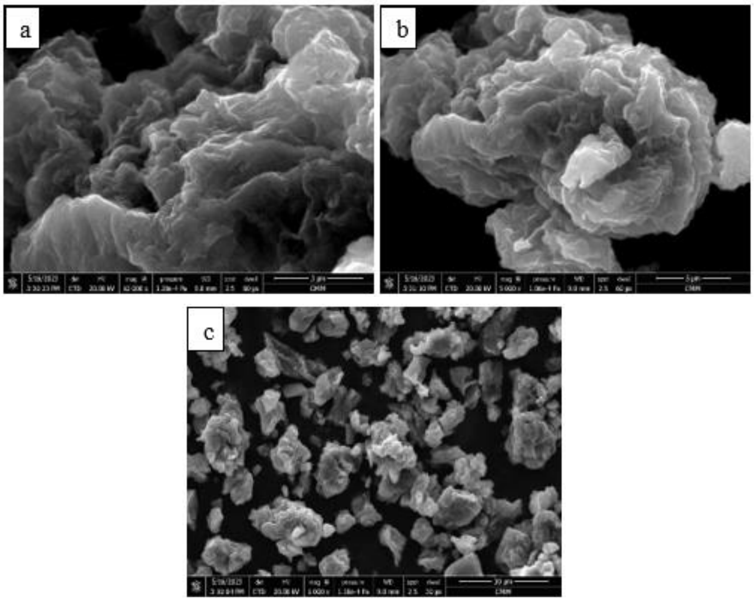

Figure 2. SEM Before Calcination, (a) 10,000x magnification, (b) 5,000x magnification, and (c) 1,000x magnification

It can also be seen in Figure 2 and Figure 3 that there is the influence of GO as a tin growth template, wherein the image after calcination, the morphology of the tin powder looks irregular because the morphology of the GO template looks crumpled so that the resulting powder is crumpled.

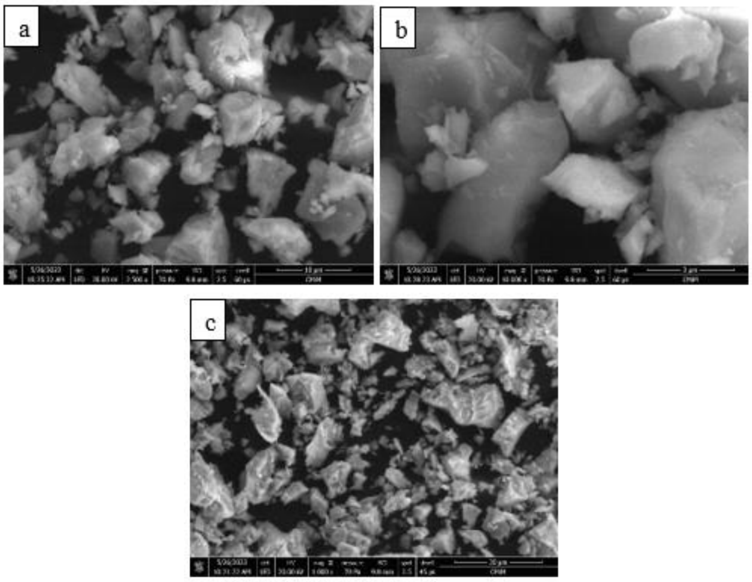

Figure 3. EM After Calcination, (a) 10,000x magnification, (b) 5,000x magnification, and (c) 1,000x magnification

It can be seen in Figure 4 that the EDS mapping results before calcination at 1,000 times magnification can show that the carbon percentage is 53.7%, which indicates the presence of the carbon element from graphene oxide (GO). In the EDS results after calcination with a magnification of 1,000 times, you can see that the carbon percentage is 21.4%, which indicates the decomposition of carbon elements during calcination, so it can be concluded that graphene oxide (GO) has been decomposed. The presence of carbon elements when carrying out EDS on samples after calcination is due to the substrate used being made of carbon elements.

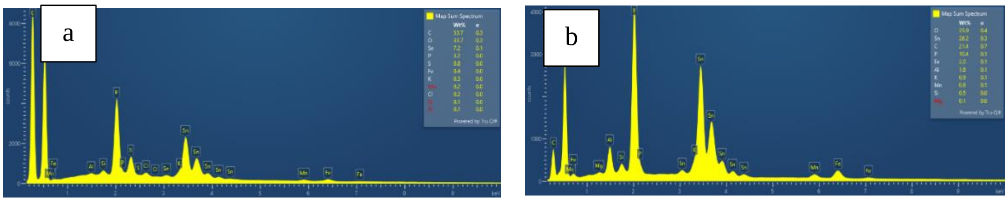

Figure 4. EDS results, (a) Before Calcination, (b) After Calcination

Results of tin phosphate/GO powder from the synthesis of electric art furnace (EAF) electrode waste graphic powder with tin powder using a modification of the Hummers method. 1 gram of tin powder with a content of 99.9% is dissolved in H_2SO_4 solution then graphite is added with a milling time of 5 hours, 10 hours, and 15 hours, with variations in adding 1 gram, 2 grams, and 3 grams of graphite after that it is synthesized with the addition of phosphoric acid (H_3PO_4) and potassium permanganate ($KMnO_4$). Next, the tin phosphate/GO powder was calcined in a furnace at a temperature of 900°C for 6 hours.

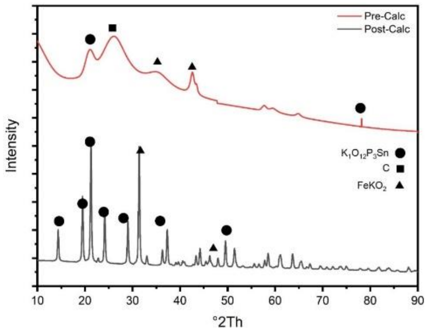

Figure 5. XRD results before calcination and after calcination

Figure 5 shows the powder XRD results before and after calcination on sample M3B3. The XRD results before calcination can be seen showing the presence of graphene oxide (GO) and potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$). This shows that graphene oxide (GO) was formed during synthesis, also the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) began to form during synthesis. It can be seen from the XRD results after calcination that there is no graphene oxide (GO) compound, showing that calcination at a temperature of 900°C for 6 hours effectively decomposes graphene oxide (GO), this is by the literature which explains that graphene oxide (GO) decomposes at a temperature of 650 °C for 2 hours (Zhao et al., 2017). It was also seen that the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with the ICSD database (98-026-1893) was formed, there was also the compound tin phosphate (SnP_2O_7) with the ICDD database (00-029-1352) and the compound potassium ferrate ($FeKO_2$) with the ICSD database (98-015-7785) after calcination.

The results of milling graphite at 5 hours, 10 hours, and 15 hours were subjected to initial characterization to determine the size distribution of graphite after milling using a particle size analyzer (PSA) so that from these results the particle size analyzer (PSA) results for graphite before milling were obtained (M0) with a z-average of 3681 nm, and a PI value of 1, then on graphite after milling for 5 hours (M¬1) a z-average of 3381 nm was obtained, and a PI value of 1, then on graphite after milling for 10 hour (M2) obtained a z-average of 2414 nm, and a PI value of 1, finally on graphite after milling for 15 hours (M3) a z-average of 2830 nm was obtained, and a PI value of 0.9359. From Figure 6, it can be seen that the trend in the initial particle size analyzer (PSA) characterization bar diagram of graphite is that there is a decrease in the particle size of the graphite before milling and after milling. However, in graphite that was milled for 15 hours (M3), there was an increase in particle size. This can occur due to several factors, namely agglomeration, when the grinding process is extended, the particles can start to clump due to high energy input, which increases particle size (Abrashev et al., 2007). Inefficient grinding, if the grinding process is not optimized, this can lead to an increase in particle size. For example, if the grinding time is too long, this can cause the particles to coalesce and form larger particles (Nasruddin et al., 2018).

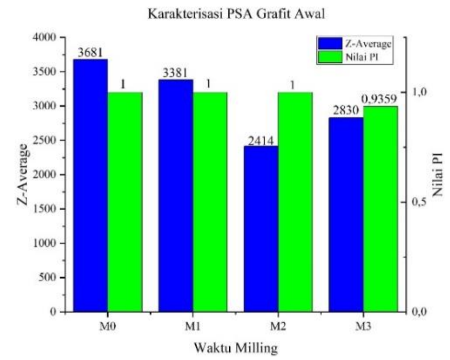

Figure 6. Graphite Size Distribution Before and After Milling

It can be seen in Figure 7 that the XRD results for sample B1 are samples with the same graphite addition ratio, namely 1 gram. In the sample with a milling time of 5 hours (M¬1B1), there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 39.57 nm, the compound tin phosphate (SnP_2O_7) with a crystal size 49.29 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 50.27 nm. In the sample with a milling time of 10 hours (M2B1) there were 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 7.70 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 6, 92 nm, potassium ferrate compound (FeKO¬2) with a crystal size of 119.16 nm, and impurities. Then in the sample with a milling time of 15 hours (M3B1) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 40.17 nm, the compound tin phosphate (SnP_2O_7) with a crystal size of 86 .31 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 88.04 nm.

The XRD results on sample B3 are samples with the same graphite addition ratio, namely 2 grams. In the sample with a milling time of 5 hours (M¬1B2), there were 3 compounds, namely, the compound potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 29.88 nm, the compound tin phosphate (SnP_2O_7) with a crystal size 51.78 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 52.83 nm. In the sample with a milling time of 10 hours (M2B2), there were 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 32.02 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 68, 02 nm, and potassium ferrate compound (FeKO¬2) with a crystal size of 69.39 nm. Then in the sample with a milling time of 15 hours (M3B2) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V))($KO_{12}P_3Sn_2$) with a crystal size of 34.68 nm, the compound tin phosphate (SnP_2O_7) with a crystal size of 74 .74 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 76.24 nm.

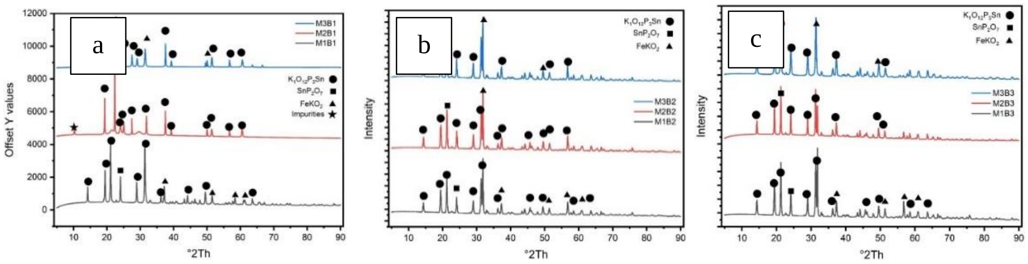

Figure 7. XRD results (a) Sample B1, (b) Sample B2, (c) Sample B3

Sample B3 is a sample with the same graphite addition ratio, namely 3 grams. In the sample with a milling time of 5 hours (M¬1B3) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 35.28 nm, the compound tin phosphate (SnP_2O_7) with a crystal size 58.87 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 60.06 nm. In the sample with a milling time of 10 hours (M2B3), there were 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 53.57 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 88, 57 nm, potassium ferrate compound (FeKO¬2) with a crystal size of 90.35 nm. Then in the sample with a milling time of 15 hours (M3B3) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 31.65 nm, the compound tin phosphate (SnP_2O_7) with a crystal size of 32 .93 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 57.95 nm.

In Figure 8 you can see a graph of the effect of milling time on the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination in sample B1. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with variations in the same weight ratio, namely 1 gram of graphite, experienced a decrease in weight from the 5-hour milling sample to the 10-hour milling sample. Meanwhile, from the 10-hour milling sample to the 15-hour milling sample, there was an increase in weight. The weight trend of the tin phosphate powder samples after calcination was an increase in weight from the 5-hour milling sample to the 10-hour milling sample. And from the 10-hour milling sample to the 15-hour milling sample there was also an increase in the sample. There is a difference in trend between the weight of the samples before and after calcination, namely in the 5-hour milling and 10-hour milling samples, where before calcination there is a decrease in weight from the 5-hour milling sample to the 10-hour milling sample, whereas after calcination there is an increase in the weight of the milling sample. 5 hours to 10 hours milling sample. It can be concluded that the amount of tin phosphate in sample M2B1 is greater than in sample M1B1. However, the M2B1 sample has less GO than M1B1, this can be proven by the weight of the M2B1 sample after calcination which is heavier than the weight of the M1B1 sample, and the weight of the M2B1 sample before calcination which is lighter than the weight of the M1B1 sample. Sample M3B1 has the highest amount of tin phosphate between sample M2B1 and sample M1B1, this is proven by the weight of sample M3B1 after calcination which is heavier than the weight of sample M2B1 and sample M1B1. However, the highest amount of GO is in sample M1B1 compared to sample M2B1 and sample M3B1, this is proven by the weight of sample M1B1 before calcination being heavier than the weight of sample M2B1 and sample M3B1.

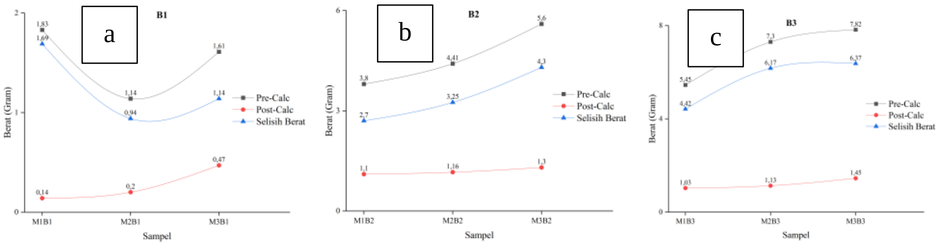

Figure 8. Weight graph before and after calcination (a) Sample B1, (b) Sample B2, (c) Sample B3

In Figure 8 you can see a graph of the effect of milling time on the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination in sample B2. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with variations in the same weight ratio, namely 2 grams of graphite, experienced an increase in weight from the 5-hour milling sample to the 10-hour milling sample. And from the 10-hour milling sample to the 15-hour milling sample there was also an increase in weight. The weight trend of the tin phosphate powder samples after calcination was an increase in weight from the 5-hour milling sample to the 10-hour milling sample. From the 10-hour milling sample to the 15-hour milling sample there was also an increase in weight. It can be concluded that sample M3B2 has the highest amount of tin phosphate and GO between sample M2B2 and sample M1B2. This is proven by the weight of the M3B2 sample before calcination and after calcination being heavier than the weight of the M2B2 sample and the M3B2 sample. In Figure 8 you can see a graph of the effect of milling time on the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination in sample B3. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with variations in the same weight ratio, namely 3 grams of graphite, experienced an increase in weight from the 5-hour milling sample to the 10-hour milling sample. From the 10-hour milling sample to the 15-hour milling sample there was also an increase in weight. The weight trend of the tin phosphate powder samples after calcination was an increase in weight from the 5-hour milling sample to the 10-hour milling sample. And from the 10-hour milling sample to the 15-hour milling sample there was also an increase in the sample. It can be concluded that sample M3B3 has the highest amount of tin phosphate and GO between sample M2B3 and sample M1B3. This is proven by the weight of the M3B3 sample before calcination and after calcination being heavier than the weight of the M2B3 sample and the M3B3 sample. From the trend in Figure 8, it can be seen that there is an influence of milling time on the weight of the powder produced before calcination and after calcination, that is, the longer the milling time, the heavier the powder produced before and after calcination. This is proven by the graphic trend of weight before and after calcination which continues to increase from a milling time of 5 hours to a milling time of 15 hours. This also indicates that there is an influence of milling time on the amount of GO and tin phosphate produced, as evidenced by the graphic trend of weight before calcination, after calcination, and the difference in weight before and after calcination which continues to increase from a milling time of 5 hours to a milling time of 15 hours. Meanwhile, in Figure 4.10, the trend is different, milling time does not affect the weight of the sample before calcination. However, after calcination, milling time affects the weight.

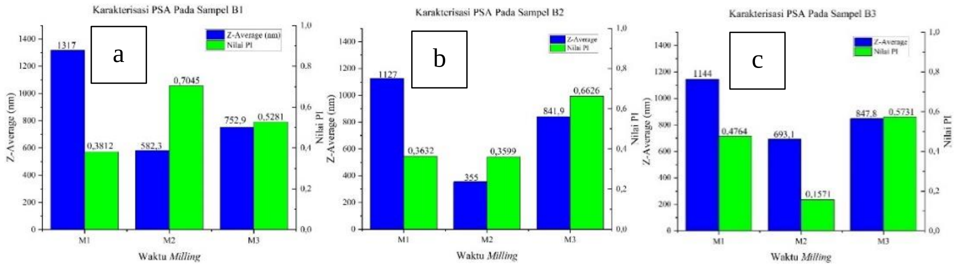

Figure 9. Size Distribution of Tin Phosphate Powder (a) Sample B1, (b) Sample B2, (c) Sample B3

From Figure 9 you can see a graph of the size distribution of tin phosphate powder with the same graphite weight ratio, namely 1 gram (B1). You can see a trend from the graph from the sample with a milling time of 5 hours to the sample with a milling time of 10 hours, there is a decrease in size. Meanwhile, from the sample with a milling time of 10 hours to the sample with a milling time of 15 hours, there was an increase in size again. However, the sample size with a milling time of 15 hours is still smaller than the sample with a milling time of 5 hours. From Figure 9 you can see a graph of the size distribution of tin phosphate powder with the same graphite weight ratio, namely 2 grams (B2). You can see a trend from the graph from the sample with a milling time of 5 hours to the sample with a milling time of 10 hours, there is a decrease in size. Meanwhile, from the sample with a milling time of 10 hours to the sample with a milling time of 15 hours, there was an increase in size again. However, the sample size with a milling time of 15 hours is still smaller than the sample with a milling time of 5 hours. From Figure 9 you can see a graph of the size distribution of tin phosphate powder with the same graphite weight ratio, namely 3 grams (B3). You can see a trend from the graph from the sample with a milling time of 5 hours to the sample with a milling time of 10 hours, there is a decrease in size. Meanwhile, from the sample with a milling time of 10 hours to the sample with a milling time of 15 hours, there was an increase in size again. However, the sample size with a milling time of 15 hours is still smaller than the sample with a milling time of 5 hours. From Figure 9, seen from the bar chart trend, all three have the same trend, namely a decrease in size from the sample with a milling time of 5 hours to the sample with a milling time of 10 hours. There was an increase in size again from the sample with a milling time of 10 hours to the sample with a milling time of 15 hours. However, the sample size with a milling time of 15 hours is still smaller than the sample with a milling time of 5 hours. It can also be seen that the three bar diagrams have the same trend as the graphite size distribution diagram before and after milling in Figure 4.6. It can be concluded that there is an influence of graphite milling time on the size of the tin phosphate powder produced. This indicates that there is an influence of the size of the GO template on the size of the tin phosphate powder produced. This is due to the theory that the template can control the shape and size of the powder (Meng et al., 2020b).

The initial weight ratio of the synthesized samples M1B1, M2B1, and M3B1 is 1 gram of tin and 1 gram of graphite, the total weight is 2 grams. The initial weight ratio for samples M1B2, M2B2, and M3B2 is 1 gram of tin and 2 grams of graphite, the total weight is 3 grams. The initial weight ratio for samples M1B3, M2B3, and M3B3 is 1 gram of tin and 3 grams of graphite, the total weight is 4 grams. It can be seen in Figure 10 that the XRD results on sample M1 are samples with the same milling time, namely 5 hours. In the sample with a graphite addition ratio of 1 gram (M¬1B1) there are 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 39.57 nm, the compound tin phosphate (SnP_2O_7) with a size crystals 49.29 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 50.27 nm. In the sample with a graphite addition ratio of 2 grams (M1B2), there are 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 29.88 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 51 .78 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 52.83 nm. Then in the sample with a graphite addition ratio of 3 grams (M¬1B3) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 35.28 nm, the compound tin phosphate (SnP_2O_7) with crystal size 58.87 nm, and potassium compound ($FeKO_2$) with a crystal size 60.06 nm.

It can be seen in Figure 10 that the XRD results on sample M2 are samples with the same milling time, namely 10 hours. In the sample with a graphite addition ratio of 1 gram (M¬2B1) there are 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 7.70 nm, the compound tin phosphate (SnP_2O_7) with a size 6.92 nm crystals, potassium ferrate compound ($FeKO_2$) with a crystal size of 119.16 nm, and impurities. In the sample with a graphite addition ratio of 2 grams (M2B2) there are 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 32.02 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 68 .02 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 69.39 nm. Then in the sample with a graphite addition ratio of 3 grams (M2B3) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 53.57 nm, the compound tin phosphate (SnP_2O_7) with a crystal size 88.57 nm, potassium ferrate compound ($FeKO_2$) with a crystal size of 90.35 nm. It can be seen in Figure 4.18 the XRD results on sample M3, namely the sample with the same milling time, namely 15 hours. In the sample with a graphite addition ratio of 1 gram (M3B1), there are 3 compounds, namely, the potassium compound ditin (IV) tris (phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 40.17 nm, the compound tin phosphate (SnP_2O_7) with a crystal size of 86 .31 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 88.04 nm. In the sample with a graphite addition ratio of 2 grams (M3B2) there were 3 compounds, namely, the potassium ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) compound with a crystal size of 34.68 nm, the tin phosphate compound (SnP_2O_7) with a crystal size of 74 .74 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 76.24 nm. Then in the sample with a graphite addition ratio of 3 grams (M3B3) there were 3 compounds, namely, the potassium compound ditin (IV) tris(phosphate(V)) ($KO_{12}P_3Sn_2$) with a crystal size of 31.65 nm, the compound tin phosphate (SnP_2O_7) with a crystal size 32.93 nm, and potassium ferrate ($FeKO_2$) compounds with a crystal size of 57.95 nm.

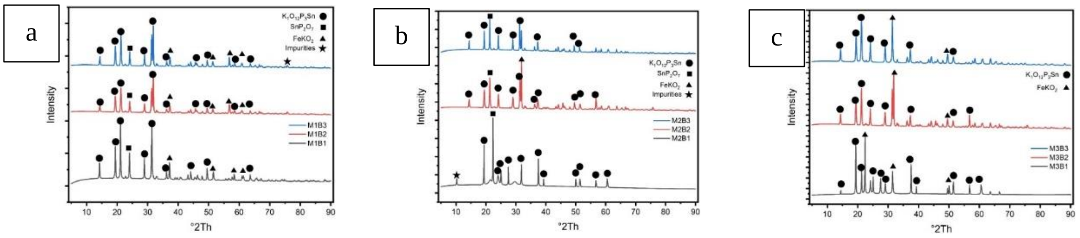

Figure 10. XRD results (a) Sample M1, (b) Sample M2, (c) Sample M3

In Figure 11 you can see a graph of the influence of the ratio of graphite weight to the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination on sample M1. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with the same milling time variation of 5 hours, there was a significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was also a significant increase in weight. The weight trend of tin phosphate powder samples after calcination showed a very significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was an insignificant decrease in weight. In Figure 11 you can see a graph of the influence of the ratio of graphite weight to the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination on sample M2. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with the same milling time variation of 10 hours, there was a significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was also a significant increase in weight. The weight trend of tin phosphate powder samples after calcination showed a very significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was an insignificant decrease in weight. In Figure 11 you can also see a graph of the influence of the ratio of graphite weight to the weight of tin phosphate/GO powder before calcination and tin phosphate powder after calcination on sample M3. Judging from the weight trend of tin phosphate/GO powder before calcination, samples with the same milling time variation of 15 hours, there was a significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was also a significant increase in weight. The weight trend of tin phosphate powder samples after calcination showed a very significant increase in weight from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was an insignificant increase in weight. As seen from Figure 11, the tin phosphate/GO sample before calcination, with a graphite addition ratio of 1 gram, the weight is between 1-2 grams. In samples with a graphite addition ratio of 2 grams, the weight was between 3-5 grams. And in samples with a graphite addition ratio of 3 grams, the weight was between 5-7 grams. In the samples with the addition of 1 gram of graphite, there was a decrease in weight, while in the samples with the addition of 2 grams and 3 grams of graphite, there was a significant increase in weight. Tin phosphate samples after calcination, the weight of samples with a graphite addition ratio of 1 gram was found to be between 0.1-0.5 grams. Meanwhile, samples with a graphite addition ratio of 2 grams and samples with a graphite addition ratio of 3 grams were found to weigh between 1 and 1.5 grams.

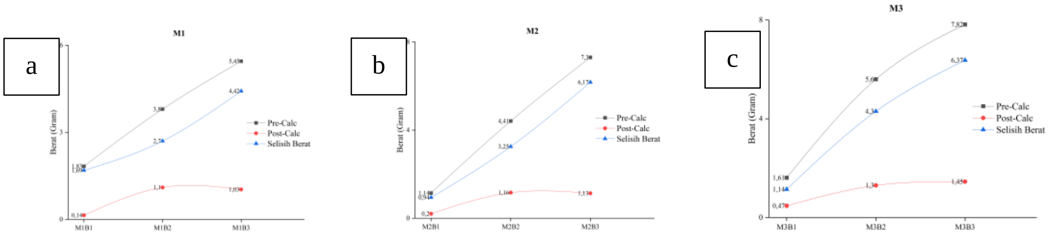

Figure 11. Weight graph before and after calcination (a) Sample M1, (b) Sample M2, (c) Sample M3

By adding the same tin, namely 1 gram of tin, in samples with a graphite addition ratio of 1 gram, you only get 0.1-0.5 grams of tin phosphate powder. Meanwhile, samples with a graphite addition ratio of 2 grams to 3 grams produced 1-1.5 grams of tin phosphate powder. This is due to the influence of the large number of GO templates as a place for tin growth and this answers the author's hypothesis. In samples with the addition of 2 grams and 3 grams of graphite, there was no significant increase or decrease in weight, this indicates that with the addition of 1 gram of tin, 2 grams of graphite is needed as a template for tin growth, which is a good ratio of Tin: Graphite for the synthesis of tin phosphate. using a modified Hummers method with GO as a template is 1:2.

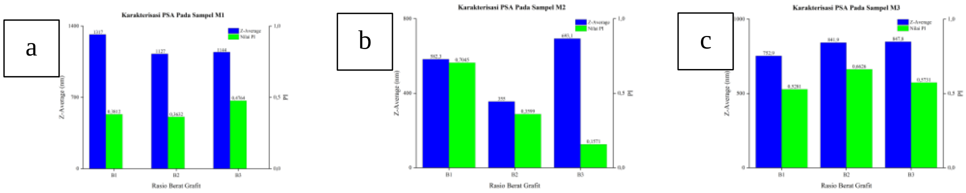

Figure 12. Graphite Size Distribution (a) Sample M1, (b) Sample M2, (c) Sample M3

From Figure 12 you can see a graph of the size distribution of tin phosphate powder with the same milling time, namely 5 hours (M1). You can see a trend from the graph from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams, there is a decrease in size. Meanwhile, from samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was an increase in size. However, the sample size with a graphite addition ratio of 3 grams is still smaller than the sample with a graphite addition ratio of 1 gram. From Figure 12 you can see a graph of the size distribution of tin phosphate powder with the same milling time, namely 10 hours (M2). You can see a trend from the graph from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams, there is a decrease in size. Meanwhile, from samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was an increase in size. The sample size with a graphite addition ratio of 3 grams is still larger than the sample with a graphite addition ratio of 1 gram. From Figure 12 you can see a graph of the size distribution of tin phosphate powder with the same milling time, namely 15 hours (M3). It can be seen from the graph that the trend is that from samples with a graphite addition ratio of 1 gram to samples with a graphite addition ratio of 2 grams, there is an increase in size. In samples with a graphite addition ratio of 2 grams to samples with a graphite addition ratio of 3 grams, there was also an increase in size.

CONCLUSION

The conclusion from research on the effect of milling time and the addition of graphite on the structure and morphology of tin phosphate powder using the graphene oxide (GO) template method for electrolyte applications that has been carried out is that the SEM results show that the morphology of the resulting powder is crumpled. It also shows the influence of GO template morphology on the morphology of the resulting powder. The results of orthorhombic. The results show that graphite milling time affects the size of the resulting powder. This also shows the influence of the size of the Graphene Oxide (GO) template on the size of the powder produced. Milling time also influences the weight of the powder produced before and after calcination. The longer the milling time, the heavier the powder. This effect also indicates the influence of milling time on the amount of GO and powder produced. The graphite addition ratio has a significant influence on the weight of the powder samples before calcination and the powder after calcination. The ratio of adding 2 grams of graphite to 1 gram of tin produces optimal powder weight after calcination, indicating the effectiveness of using GO as a tin growth template.

REFERENCES

Abrashev, B., Bliznakov, S., Spassov, T., & Popov, A. (2007). Electrochemical hydriding of nanocrystalline TiFe alloys. *Journal of Applied Electrochemistry*, *37*(7), 871–875. https://doi.org/10.1007/s10800-007-9322-4

Ardhi, R. P. (2022). *Pengaruh Ukuran Serbuk Grafit Dan Media Pelarut Dispersi Pada Metode Sintesis Sno2@Go Terhadap Struktur Dan Morfologi Serbuk Timah Oksida Untuk Aplikasi Sensor Gas Skripsi*. Sultan Ageng Tirtayasa University.

Bhagwat, A. D., Sawant, S. S., Ankamwar, B. G., & Mahajan, C. M. (2015). Synthesis of Nanostructured Tin Oxide (SnO2) Powders and Thin Films by Sol-Gel Method. *JOURNAL OF NANO- AND ELECTRONIC PHYSICS*, *7*(4), 4037.

Catur, U., Yudhatama, D., & Mukhoriyah. (2015). Identifikasi Lahan Tambang Timah Menggunakan Metode Klasifikasi Terbimbing Maximum Likelihood Pada Citra Landsat 8 (Identification of Tin Mining Area Using Maximum Likelihood Supervised Classification on Landsat 8 Image). *Majalah Ilmiah Globë*, *17*(1), 009–015.

Meng, Z. C., Gao, L. Y., & Liu, Z. Q. (2020a). Synthesis of Sn nanowire by template electrodeposition and its conversion into Sn nano solder. *Materials Characterization*, *163*. https://doi.org/10.1016/j.matchar.2020.110278

Meng, Z. C., Gao, L. Y., & Liu, Z. Q. (2020b). Synthesis of Sn nanowire by template electrodeposition and its conversion into Sn nano solder. *Materials Characterization*, *163*. https://doi.org/10.1016/j.matchar.2020.110278

Nasruddin, M. N., Khairuman, T., Sebayang, P., Sebayang, K., Ginting, Y. A., & Noer, Z. (2018). Study of Particle Size and Affix Fe in Permanent Magnet Materials BaFe 12 O 19 against Their Physical Properties. *Journal of Physics: Conference Series*, *1116*(3). https://doi.org/10.1088/1742-6596/1116/3/032021

Pei, L., Jin, Q., Zhu, Z., Zhao, Q., Liang, J., & Chen, J. (2015). Ice-templated preparation and sodium storage of ultrasmall SnO2 nanoparticles embedded in three-dimensional graphene. *Nano Research*, *8*(1), 184–192. https://doi.org/10.1007/s12274-014-0609-6

Prodjosantoso, A. K., L.F.X., E. W., & Utomo, M. P. (2011). Sintesis Dan Karaterisasi Sno2 Sebagai Upaya Pengembangan Produk Hilir Timah Putih Untuk Meningkatkan Devisa Nasional. *Jurnal Penelitian Saintek*, *16*(2).

Shaalan, N. M., Hamad, D., Abdel-Latief, A. Y., & Abdel-Rahim, M. A. (2016). Preparation of quantum size of tin oxide: Structural and physical characterization. *Progress in Natural Science: Materials International*, *26*(2), 145–151. https://doi.org/10.1016/j.pnsc.2016.03.002

Suharyanto, A., & Hanum Lalasari, L. (2016). *Potensi Mineral Kasiterit Indonesia Sebagai Bahan Baku Pembuatan Senyawa Kimia Timah (Tin Chemical).*

Surya, K., & Yusuf, M. (2020). *Potensi Investasi Tin Can Dalam Peningkatan Nilai Tambah Logam Timah Bangka Belitung Potential Of Tin Can Investment To Increase Value Of Tin Metal In Bangka Belitung*. *4*(2).

Tang, B., Gao, E., Xiong, Z., Dang, B., Xu, Z., & Wang, X. (2018). Transition of Graphene Oxide from Nanomembrane to Nanoscroll Mediated by Organic Solvent in Dispersion. *Chemistry of Materials*, *30*(17), 5951–5960. https://doi.org/10.1021/acs.chemmater.8b02083

Zhao, H., Zhu, Y., Li, F., Hao, R., Wang, S., & Guo, L. (2017). A Generalized Strategy for the Synthesis of Large-Size Ultrathin Two-Dimensional Metal Oxide Nanosheets. *Angewandte Chemie - International Edition*, *56*(30), 8766–8770. https://doi.org/10.1002/anie.201703871