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Synthesis of Cathode Active Material $LiMn_{0.5}Fe_{0.5}PO_4F/C$ with Sintering Time Variation

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Abstract. Research has been carried out on the synthesis of $LiMn_{0.5}Fe_{0.5}PO_4F/C$, the cathode active materials with variations in sintering time. The process of producing the $LiMn_{0,5}Fe_{0,5}PO_4F/C$ as an active material in lithium battery cathodes has been successfully carried out by the first forming host structure and then infiltrating the lithium Li ions and the flour F ions. In this study, the synthesis was carried out with various sintering time, 6 hours, 8 hours and 10 hours. The raw materials used in this study are manganese dioxide ("MnO_2"), iron (III) oxide ("Fe_2O_3"), lithium fluoride ("LiF") and phosphoric acid ("H_3PO_4") as the solvents. The synthesis was carried out at a calcination temperature of 720°C for 8 hours. The first mashed use a milling process for about 180 minutes, and placed into the oven, then mashed using a mortar. Then the $Mn_{0.5}Fe_{0.5}PO_4$ sample was added with LiF, mixed with the milling process, placed into a drying oven and was varied with the sintering time of 6 hours for the first sample, 8 hours for the second sample and 10 hours for the third sample. As to produce $LiMn_{0.5}Fe_{0.5}PO_4F$ material, followed by carbon coating, namely tapioca and sugar (8%:4%). All three samples were calcined at a temperature of 720°C for 4 hours. The results of XRD analysis showed that the three samples did not experience a phase of change, however only shows a few differences in intensity. The results of FESEM analysis show that grain growth occurs vertically and horizontally due to the presence of the Mn and Fe, and with an exact enough amount of tapioca function as a carbon source to coat the active material, it help to creates pores in the powder so that the presence of these pores could provide an intercalation pathway for the lithium ions. At the end the results of the EIS analysis showed that the highest conductivity value of this study was 0.62×10^{-5} S/cm.

Keyword: Cathode Material, Characterization, Li-Ion Battery, Variation of Sintering Time.

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1 Introduction

Technological developments at this time all electronic components require an energy source, especially in the field of electrical energy that goes portable-based. Many electronic devices require batteries as an energy source for portable electronic devices. Batteries are one of the electronic components that can convert chemical energy into electricity. A battery or accumulator is an electrical cell in which reversible electrochemical processes take place with

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high efficiency. Reversible electrochemical reactions are found in batteries that take place the process of converting chemicals into electric power (emptying process) and vice versa from electric power to chemical power (charging process) by means of the process of regeneration of the electrodes used that is by passing the electric current in the opposite polarity in the cell [1]. The active electrode in a Lithium-ion battery is lithium metal oxide for the positive electrode while the carbon on the electrode is negative. This material adheres to a metal collector current with a binding material, usually in the form of polyvinilidene flouride (PVDF) or polyvinilidene polyvinyldene hydrolymer fluoride-hexafluoropropylene (PVDF-HFP), and conductive penencer [2]. Therefore, portable electrical energy (battery) will play an important role in the development of technology in the future. One type of battery that is currently being widely developed is lithium batteries. Lithium batteries are one of the solutions as an energy store and contribute to reducing the effects of global warming (green-house gases). In its development to date, the use of batteries is very inseparable from everyday life. Almost all electronic devices use batteries as a storage source for energy [3]. Lithium batteries are already circulating in the market to meet the needs of batteries in the computer industry, military communication devices, mobile phones, lighting devices, cameras, handycams and cars. The development of cars that occurred until now makes cars can be divided into three, namely conventional cars (ordinary), mobilhybrid (Hybrid Electric Vehicle) and electric cars. Lithium batteries have usage optimization up to 80% of their capabilities, lightweight, no memory effect and long-lasting [4].

One of the cathode materials that is currently starting to be widely developed, namely olivine type cathodes such as $LiMnPO_4$ and $LiFePO_4$. $LiMnPO_4$ cathode has the same theoretical capacity as $LiFePO_4$ cathode which is about 170 mAh/g. $LiMnPO_4$ has a relatively higher working potential that is close to 4 V when compared to $LiFePO_4$ which only ranges from 3.5 V. $LiMnPO_4$ material properties have higher energy density and lower production costs than $LiFePO_4$. $LiMnPO_4$ cathode also has good thermal stability, is environmentally friendly, and is safe to use as a promising cathode material for future battery systems. The disadvantage of this cathode is that its electronic conductivity and ionic conductivity values are much lower (<10-10 Cm/s) compared to $LiFePO_4$ (1.8×10-9 S/cm). This leads to the electrochemical properties and low rate of diffusion of lithium ions. Lithium ion batteries operate based on the movement of lithium ions, so the cathode material in lithium batteries must have high ion conductivity to be able to deliver lithium ions quickly [5]. Several studies have been conducted to improve the electrical conductivity of $LiMnPO_4$, including coating with carbon, substitution of some transition metals or doping with other transition metals, and optimization of particle size and morphology. In this study, improvement of the form of carbon coating will be done so that the carbon layer has pores, and the electrolyte fluid can touch the cathode active ingredient directly through the pores formed and make it easier for lithium ions to migrate. Mn manganese transition metal affects the coating to develop horizontally, so the coating will cover the entire surface of the cathode active material. The transition metal phero/Fe iron has a tendency to direct the development of carbon coating vertically, so that carbon coating develops by not covering the entire surface of the cathode active material [6].

This research will make the cathode active ingredient with the same concentration of phero/iron transition metals Fe and manganese Mn. In this study the time of sintering will be varied to see the effect of the development of carbon layer growth. Analysis of the growth of carbon layers is carried out morphological observations in nanometers with FESEM test equipment and its effect on the conductivity of cathode active ingredients in EIS. Based on the description above, research is needed on $LiMnFePO_4F/C$ with variations in sintering time at the time of addition of lithium which is 6, 8 and 10 hours. In this study one way to increase the conductivity of lithium batteries from $LiMnFePO_4F/C$ material by coating the active material with carbon namely tapioca and sugar. Carbon coating is one of the most important techniques for increasing electrical conductivity in lifepo4 cathode active materials. In general, carbon (C) has an electrical conductivity of 10 S/cm [7]. Tapioca has advantages such as easy to obtain, relatively cheap price, and high carbon content [8]. There are tapioca and sugar contain a lot of carbon with the chemical formula $C_6H_{10}O_5$ and sugar $C_{12}H_{22}O_{11}$. Coating using carbon from organic compounds is expected to overcome the problem of electrical conductivity &production costs. The source of carbon that can be used to coat the sample is tapioca because in addition to the increase in high electrical conductivity is also easy to obtain [9].

2 Materials and Methods

The materials used in the study were MnO_2, Fe_2O_3, H_3PO_4, LiF, Tapioca and Sugar, PVDF (Polyvinylidene fluoride), Super P, NMP (N-methyl-2-pyroolidon), separator, Lithium Metal and $LiPF_6$. The process of making materials begins by weighing all raw materials according to the results of stoichiometric calculations using a digital balance sheet. With MnO_2 = 16.9650 grams, Fe_2O_3 = 15.6098 grams, HPO_4 = 38.22 grams to get $MnFePO_4$ weighing 60 grams. The material that has been weighed is mixed first by stirring. After the ingredients are mixed well, the ingredients are dried in the oven and then grinding. After that, sintering with a temperature of 720°C for 8 hours with an initial temperature of 0°C under the atmosphere of nitrogen. And $MnFePO_4$ material is re-weighed, the final result divided by 3 to get the variation in sintering time.

After the material $MnFePO_4$ is divided into 3, then added three samples with the mass of each sample, namely, LiF = 2.5088. $LiMnFeCoPO_4$, PVDF, Super P active materials are weighed using digital balance sheets, while for NMP is measured using beaker glass. The mass of the active ingredient $LiMnFePO_4$ with each sintering time variant takes as much as 0.5 grams each. PVDF mass takes as much as 8% of the mass of the active ingredient, Super P mass takes as much as 2% of the mass of the active ingredient and NMP solvent as much as 1.5 mL for each sample of 6 hours, 8 hours, and 10 hours. NMP and PVDF solvents are inserted into Beaker Glass, then inserted magnetic stirrer in it. Placed the beaker glass on top of the Hot Plate. Hot

Plate settings with 700 rpm and temperature 70°C. Then wait for 30 minutes until evenly mixed. After that inserted Super P using a spatula and wait for 30 minutes until the Super P powder is mixed evenly and the color becomes black. Then inserted powder active ingredient $LiMnFePO_4$ slowly using a spatula awaited for 30 minutes until evenly mixed and the resulting color is also black.

After the material is finished formed into a slurry, then the material is ready to be made into cathode sheets. The tool used is Doctor Blade. Doctor Blade is cleaned using acetone and then the precision of the Doctor Blade gap is set to a thickness of 200 μm. Al Foil is cleaned using acetone. Al Foil sheets are placed on top of the coating machine and the vacuum button is turned on. Pour the slurry over the Al Foil, then using Doctor Blade, the slurry is flattened on the Al Foil sheet according to the specified thickness. After the coating process is complete, the cathode sheet is lifted and dried using the oven at 80°C until dry. The same step is done for active ingredients with variations in sintering time of 6 hours, 8 hours and 10 hours. The cathode sheet that has been formed is cut into a circle with a diameter of 15 mm and the separator is cut with a size of 19 mm. At this stage, the $LiMnFePO_4$ cathode sheet that has been prepared in the form of coin cells is assembling in the Glove Box with anode that is lithium metal, electrolyte that is $LiPF_6$ and separator as a separator between cathode and anode that serves to prevent a short connection between cathode and anode. Assembling inside the Glove Box aims to keep all materials from being contaminated with outside air. Then after becoming a coin battery, EIS testing is carried out on the battery. And characterized using X-Ray Diffraction (XRD) tools, Field Emission Scanning Electron Microscopy (FESEM).

Conductivity calculations are performed by interpreting the size of the bow. This calculation will get the impedance value of $R_{material}$ and R_{ion}. The $R_{material}$ value indicates the characteristics of the material which is ohmic, while R_{ion} exhibits qualitative characteristics of ion transfer between electrodes. Rbahan characteristics are always seen in high-frequency data, while Rion is observed at low frequencies [10]. To get the R_{tot} value, we must get $Z" = 0$ by extrapolating to form a semicircular. R_{tot} is the sum of $R_{material}$ and R_{ion} From this $Z = R_{tot}$ value, we can determine the conductivity of materials by using the equation

$$\sigma = \frac{t}{R_{tot} \times A} \tag{1}$$

and,

$$R_{tot} = R_{material} + R_{ion} \tag{2}$$

where, t is sample thickness (cm), A is sample surface area (cm^2), $R_{material}$ is material resistance (Ω), R_{ion} is ion resistance (Ω), R_{tot} is resistance of materials and ions (Ω), and σ is conductivity (S/cm).

3 Result and Discussion

3.1 XRD Test Results

Identification of the highest peak list which is the characteristic peaks of a sample is done by testing X-Ray Diffraction (XRD) with The Rigaku Brand with Cu Kα radiation. If the characteristic peaks of $LiMnPO_4$ and $LiFePO_4$ appear, then the crystal phase can be identified. The XRD data analysis process is carried out using softwere Match to determine the highest phase and peak formed in the $LiMn_{0,5}Fe_{0,5}PO_4F/C$ powder mixture sample.

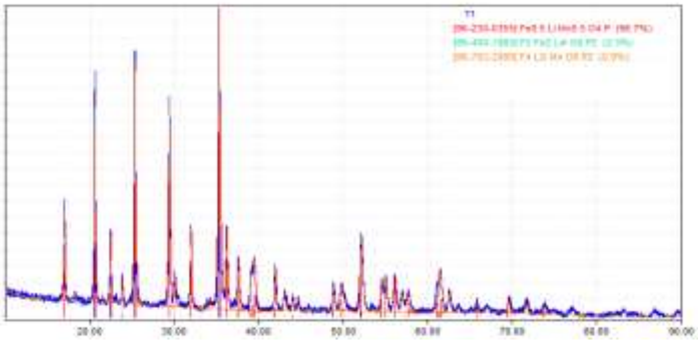


Figure 1. Sample XRD Result Graph with 6 hours Sintering Time

Based on these data, there are 3 phases formed, namely, $Fe_{0.5}LiMn_{0.5}O_4P$ with a percentage of 96.7% ; $F_2Fe_2Li_4O_8P_2$ with a percentage of 2.3% ; and $F_4Li_3MnO_6P_2$ with a percentage of 0.9%. In this sample, a scattering angle of 2θ has the highest peak at an angle of 35.390. With a crystal spacing of 2.5343 Å, FWHM 0.2800 sec and an intensity of 1000 cps.

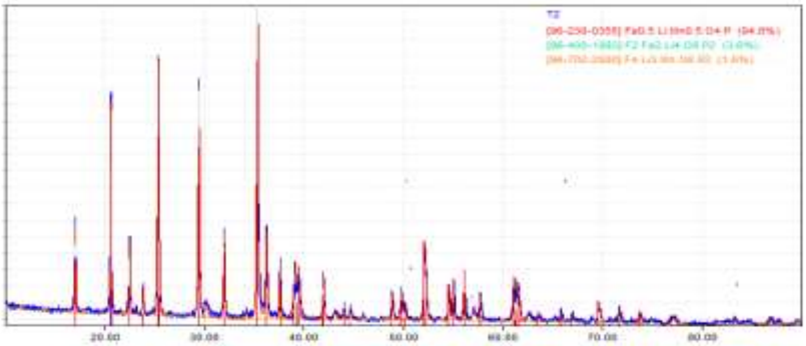


Figure 2. Sample XRD Result Graph with 8 hours Sintering Time

From the data there are 3 phases formed, namely, $Fe_{0.5}LiMn_{0.5}O_4P$ with a percentage of 94.8% ; $F_2Fe_2Li_4O_8P_2$ with a percentage of 3.6% ; and $F_4Li_3MnO_6P_2$ with a percentage of 1.6%. In this sample, a scattering angle of 2θ has the highest peak at an angle of 35.350. With a crystal spacing of 2.5371 Å, FWHM 0.1600 sec and an intensity of 1000 cps.

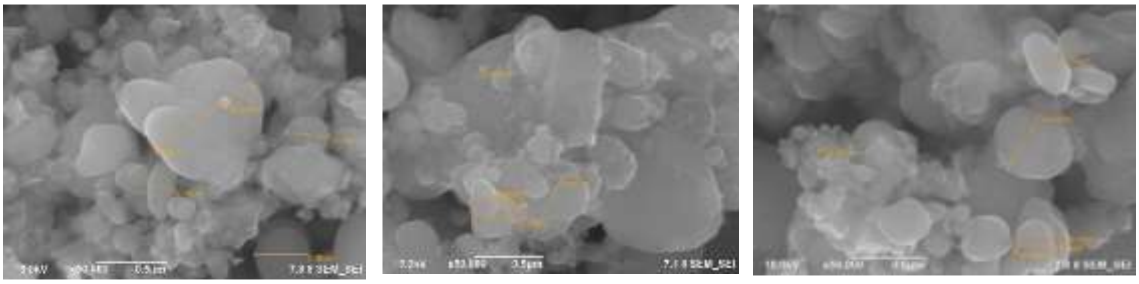
Figure 3. Sample XRD Result Graph with 10 hours Sintering Time

From the data there are 3 phases formed, namely, $Fe_{0.5}LiMn_{0.5}O_4P$ with a percentage of 74.4%; $F_2Fe_2Li_4O_8P_2$ with a percentage of 0.8% ; and $F_4Li_3MnO_6P_2$ with a percentage of 24.8%. In this sample, a scattering angle of 2θ has the highest peak at an angle of 35.350. With a crystal spacing of 2.5371 Å, FWHM at 0.1800 sec and an intensity of 1000 cps.

From the three charts, it is not clearly visible the shift of each peak. From the results of the analysis of the three samples, it can be seen that the phases can be the same and do not experience phase changes. There was only a slight difference in intensity from the three samples.

3.2 FESEM Characterization

FESEM (Field Emission Scanning Electron Microscopy) analysis was tested to determine the morphological shape of the constituent particles of cathode material. The sample observed was a sample of $LiMn_{0.5}Fe_{0.5}PO_4F/C$ at a calcination temperature of 720°C. Observations on the sample were carried out with magnification of 50000 times magnification.



(a) (b) (c)

Figure 4. Microstructure of Powder Surface with Sintering Time 6 hours, (b) 8 hours, (c) 10 hours

It can be seen that the growth of granules in the third sample occurs vertically and horizontally with enough tapioca which serves as a source of carbon to coat the active material that causes pores in the powder, pores of different sizes, but evenly distributed so that the pores can provide an intercalation pathway for lithium ions.

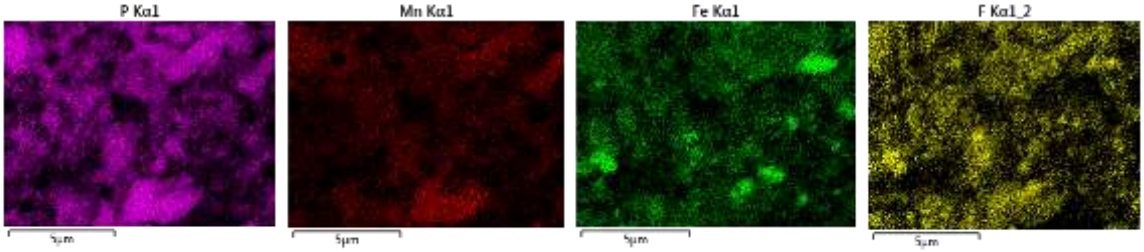


Figure 5. Sample Mapping Results with Sintering Time of 6 hours

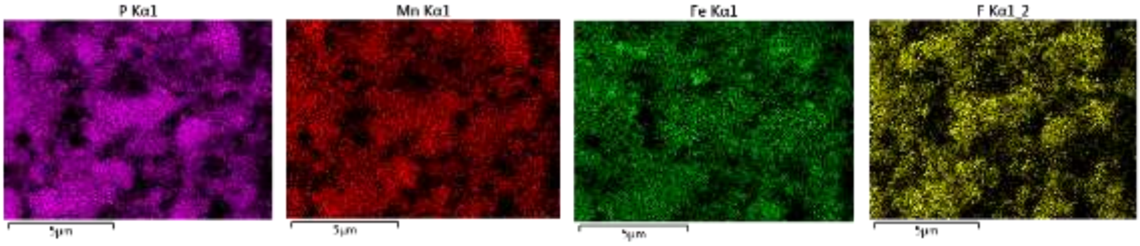


Figure 6. Mapping Results with 8 hours Sintering Time

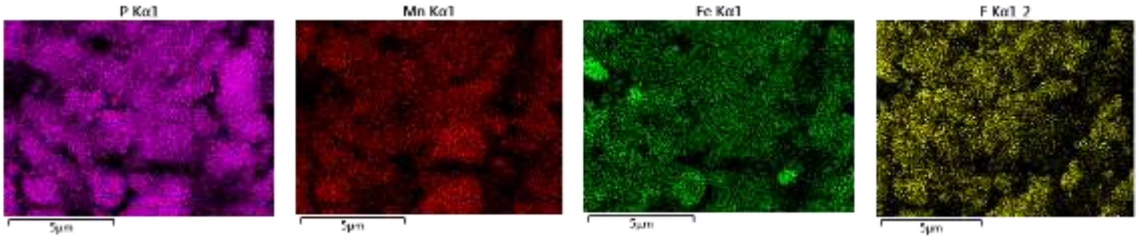


Figure 7. Mapping Results with 10 hours Sintering Time

Based on the figure for each sample, it can also be seen that the mixing of active materials occurs evenly as evidenced by the mapping results of each element. Where the elements Fe, Mn, P, and O are in all parts. All three samples were mixed homogeneously and all three samples had pores that formed but had differences in the particle size. In the second sample the grains are slightly finer than the first and third samples.

3.3 Electrochemical Impedance Spectroscopy (EIS) Testing

In this study, the EIS test tool was used to determine the magnitude of conductivity of each sample. The results of the analysis of cole plot graph images can be analyzed using a semicircle. To get the R_{tot} value, then we must get $Z" = 0$ by extrapolating to form a semicircle. R_{tot} is the sum of $R_{material}$ and R_{ion}.

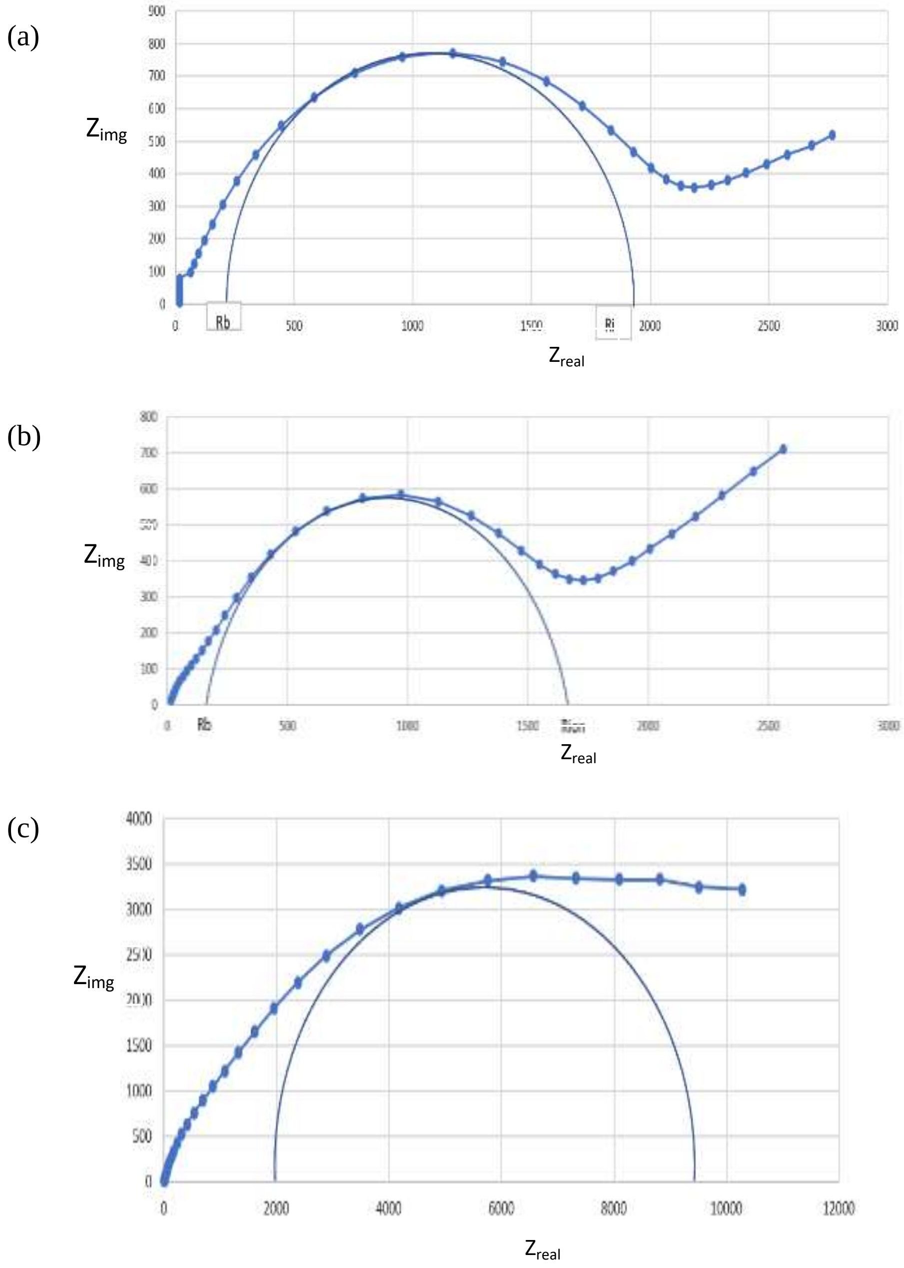


Figure 8. Graph of EIS test results (a) sintering time of 6 hours, (b) 8 hours, (c) 10 hours

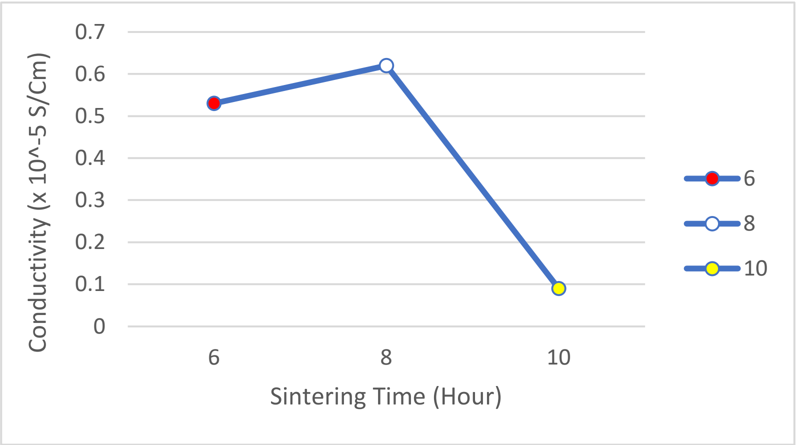


Figure 9. Conductivity vs Sintering Time Comparison Graph

Tabel 1. Comparison of conductivity values and sintering time of samples

Sample	Sintering Time (hours)	σ (10^{-5} S/cm)
Sample 1	6 hours	0.53
Sample 2	8 hours	0.62
Sample 3	10 hours	0.09

Based on the results of the analysis and calculations above, it can be concluded that the highest conductivity is found in the second sample with an 8-hour sintering length of 0.62×10^{-5} S/cm. This can be seen based on the ion conductivity value of each sample, which shows that the highest ion conductivity is also in the second sample, which is 0.62×10^{-5} S/cm and the lowest conductivity was in the third sample with a time variation of 10 hours of sintering which is 0.09×10^{-5} S/cm.

Based on the graph can be seen from the first sample with a time of 6 hours sintering experienced an increase in conductivity to the second sample with a time of 8 hours of sintering. But in the third sample with a sintering time of 10 hours experienced a decrease in conductivity value. This is because at the time of sintering 10 hours the active material of the cathode that undergoes combustion results in the sample undergoing a phase change from solid to gas. This condition causes the composition of the active material to decrease and affect its conductivity value.

4 Conclusion

The process of making $LiMn_{0.5}Fe_{0.5}PO_4F/C$ as a lithium battery cathode active material has been successful by forming the host structure first and then infiltrating lithium ions Li and ion flour F. XRD analysis results show that all three samples are in the one-phase structure of $LiFe_{0.5}Mn_{0.5}PO_4$ with flour F in the field of $F_2Fe_2Li_4O_8$ and $F_4Li_3MnO_6P_2$. The XRD patron of each sample is the same and the phase formed is also one, there is no change. The results of conductivity testing using the EIS tool, it can be concluded that the comparison of each sample $LiFe_{0.5}Mn_{0.5}PO_4F/C$ for variations in sintering time of 6 hours has a conductivity of 0.53×10^{-5} S/cm, for variations in sintering time of 8 hours has a conductivity of 0.62×10^{-5} S/cm and for the variation of sintering time of 10 hours has a conductivity of 0.09×10^{-5} S/cm. In the variation in sintering time, the highest total conductivity value was in the sample with a variation of 8 hours of sintering time of 0.62×10^{-5} S/cm. The resulting morphological structure is the growth of granules in morphology with particles that have pores. Grain growth occurs vertically and horizontally due to the influence of the composition of Fe and Mn. Based on the results of FESEM mapping it can be seen that the shape of the particle surface appears homogeneous.

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