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# Synthesis of $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$ Compound Using the Solvothermal-Microwave Irradiation Method

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**Abstract.** This research was conducted to synthesize  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) using the combination of solvothermal-microwave irradiation method and to analyze the characteristics of  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  including their crystal structures, space groups, lattice parameters, and morphologies. Characterizations of  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) were carried out using X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) Spectroscopy techniques.  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  crystal structures were analyzed by refining the XRD data with U-Fit program.  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) were successfully synthesized using solvothermal-microwave irradiation method. Based on the XRD analysis, the characterization shows that  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) formed are types of crystalline which are not so pure. Crystal size analysis shows a decrease as mole  $x$  ratio increases. The crystal structure analysis obtains orthorhombic crystal with  $Pnma$  space group. The lattice parameter decreases along with the increasing mole ratio  $x$ . The oxidation states of Fe, P, O and Cr were found to be  $2+/3+$ ,  $5+$ ,  $2+$  and  $3+$ , respectively as revealed by X-ray Photoelectron Spectroscopy. The results of SEM-EDX analysis shows that the addition of Cr-doping works as proven by the EDX result in  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$ .

## INTRODUCTION

In this day, the development of technology for energy storage is growing rapidly. Various studies to develop batteries with a very large capacity have been carried out. The invention of batteries with large capacity goes along with the development of electrodes in them. The increasing number of human needs for energy and the development of electronic devices requiring energy storage leads to various innovations to develop electrodes in batteries. Lithium-ion batteries are the most widely used batteries nowadays.

The advantage of using lithium-ion batteries is that they relatively last longer-around 500-1000 cycles and have high voltage, high energy density, as well as a higher specific capacity compared to other batteries. Lithium batteries are used in a variety of electronic devices and are able to store a greater energy capacity compared to other types of batteries. This battery type is developed for electric cars with larger capacities [1].

One of the advantages of using  $\text{LiFePO}_4$  cathode is that it has a high theoretical specific capacity (170 mAh/g), low synthesis cost, environmentally friendly synthesis, and good thermal safety. However, its performance is significantly hampered by the slow rate of lithium-ion. The rate performance of lithium ions and  $\text{LiFePO}_4$  capacity can be improved by coating carbon or metal conductive layers, doping using isovalent ions or reducing the size of particles to nanoparticles. Various methods have also been developed to synthesize the nanostructure of  $\text{LiFePO}_4$  particles, including the solvothermal method [2].

The electronic conductivity can be increased by coating the batteries with carbon or transition metals. In addition, the diffusion rate of  $\text{Li}^+$  ions and the amount of lithium from  $\text{LiFePO}_4$  can be manipulated by synthesizing a grain size compound into its nano size, as well as by adding transition metals. Maximizing the performance of  $\text{Li}^+$  in  $\text{LiFePO}_4$  particles and adding transition metals to the compound are the most possible methods to develop  $\text{LiFePO}_4$  with better performance. This strategy increases the electronic capacity and conductivity simultaneously [3]. The electrochemical performance of  $\text{LiFePO}_4$  doped with Cr(III) is much better than that of  $\text{LiFePO}_4$  doped with metal M(II) ( $M = \text{Mg}, \text{Cu}, \text{Zn}, \text{Ni}$ ) [4]. Park (2011) synthesized  $\text{LiFe}_{1-x}\text{Cr}_x\text{PO}_4$  by adding chromium doping which resulted in materials with excellent ion diffusion rates. The improved rate performance is associated with cation cavities in  $\text{LiFePO}_4$  produced by chromium doping, in addition, to improve lithium-ion rate performance, chromium doping is added to facilitate the migration of lithium ions in  $\text{LiFePO}_4$ . Shin (2008) conducted research on chromium doping on  $\text{LiFePO}_4/\text{C}$  synthesized through a one-mechanochemical process. It was found that  $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$  had a very good performance, and the sample provided a capacity of 120 mAh/g. It indicates that chromium doping facilitates phase transformation between triphylite and heterosite during the cycling process [5].

The solvothermal-microwave irradiation method shows a faster reaction than the conventional solvothermal method. The use of microwave irradiation in the solvothermal method can evenly distribute the heat under constant pressure so that a faster reaction is in place [6]. The advantage of using solvothermal-microwave irradiation is the production of more controlled particle sizes in a relatively shorter time [7-8]. This microwave irradiation assisting solvothermal synthesis becomes one of the innovations in Green Chemistry that provides short reaction times and more efficient energy than the conventional solvothermal synthesis does.  $\text{LiFePO}_4$  compound obtained from solvothermal synthesis shows good morphology. Samples prepared in ethylene glycol solvents show a theoretical capacity of 118 mAh/g at a current density of  $0.1 \text{ mA}/\text{cm}^2$  [9].

## EXPERIMENTAL SECTION

### Synthesis of $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$

The  $\text{Fe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) compounds are synthesized through a two-stage reaction of solvothermal-microwave irradiation by dissolving  $\text{Fe}(\text{CH}_3\text{COO})_2$  (Aldrich) into ethylene glycol (Aldrich-Sigma) and  $\text{H}_3\text{PO}_4$  (Merck) is dissolved in ethylene glycol. Doping  $\text{Cr}(\text{CH}_3\text{COO})_3$  (Aldrich) in ethylene glycol is added based on mole ratio calculations. Acetic acid (Merck) is put into the mixture to avoid the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in the open air. The precursors are put in the autoclave teflon and irradiated in a microwave for 2 hours. The precipitate is then filtered and dried in an oven for 1 hour and then calcinated for 2 hours. After this process,  $\text{LiOH}$  is out into the white  $\text{Fe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  precipitate the formed compound is dried in an oven for 1 hour before being calcinated for 4 hours at  $750^\circ\text{C}$ . The  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  synthesis scheme is shown in Figure 1

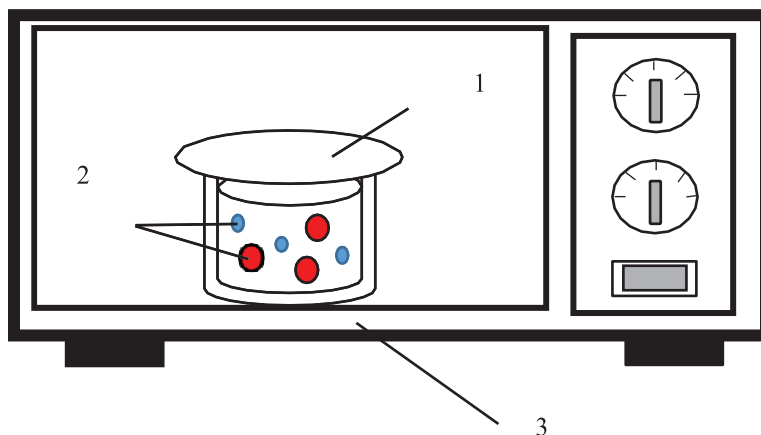


FIGURE 1. The Solvothermal-Microwave Irradiation Method Scheme, (1) autoclave Teflon, (2) Precursor, (3) Microwave

## Characterization of $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$

Characterization of  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) compound were analyzed using X-ray diffraction (XRD) employing the Rigaku 600 miniflex. The compound underwent X-ray photoelectron spectroscopy (XPS) analysis to calculate the valence states of Li, Fe, P, O and Cr using Thermo VG Scientific instrument, Multilab 2000. Then, scanning was done using Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) employing Jeol JED-2300. The qualitative data in this research were obtained in the form of X-ray spectra from XRD. X-ray diffraction was done using  $\text{Cu K}\alpha$  monochromatic radiation with wavelengths ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of  $2\theta$  between  $10^\circ$  to  $70^\circ$ . The characterization using SEM-EDX aimed to determine the morphology of the compound formed and its composition

## RESULTS AND DISCUSSION

$\text{LiFePO}_4$  and  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0.01; 0.03; 0.05; 0.1$ ) have been successfully synthesized through a two-stage reaction. The first stage is the formation of  $\text{Fe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  using the solvothermal-microwave irradiation method for 2 hours at medium temperature. The second stage is performed through the lithiation process by heating at  $750^\circ\text{C}$  for 2 hours to get a reddish-white compound. The result of the synthesis with a single-stage reaction tends to show the characteristics of the  $\text{FePO}_4$  compound with a space group ( $P3_121$ ) Pdf Card No. 9012512. It is somehow different from the compound formed using the two-stage reaction. The diffraction pattern shown in the two-stage reaction process implies the formation of the  $\text{LiFePO}_4$  compound. However, the compound shows that it goes through other phases, especially in the XRD diffractogram peaking at  $2\theta$  that has considerably high intensity. Another phase in the compound is  $\text{FePO}_4$  which does not undergo lithiation due to lack of energy. The space group of the compound synthesized through the two-stage is similar to the characteristics of the  $Pnma$  space group [10]. Through a two-stage reaction, the research produced an iron metal that was doped with chromium in the first stage [11]. The formula is obtained theoretically using aliovalent doping on the  $\text{LiFePO}_4$  compound. The solid solution mechanism with the addition of substitution of atoms or ions with a higher valence forms cation or interstitial anion vacancies. In the synthesis of the  $\text{LiFePO}_4$  compound,  $\text{Cr}^{3+}$  ion doping is used, theoretically, a cation vacancy is formed in the non-stoichiometric formula symbolized by  $V_x$  (vacancies) at the  $\text{Fe}^{2+}$  site. The crystal lattice parameter was obtained by analyzing  $hkl$  field processes performed using the U-Fit program. The XRD diffraction pattern is shown in Figure 2.

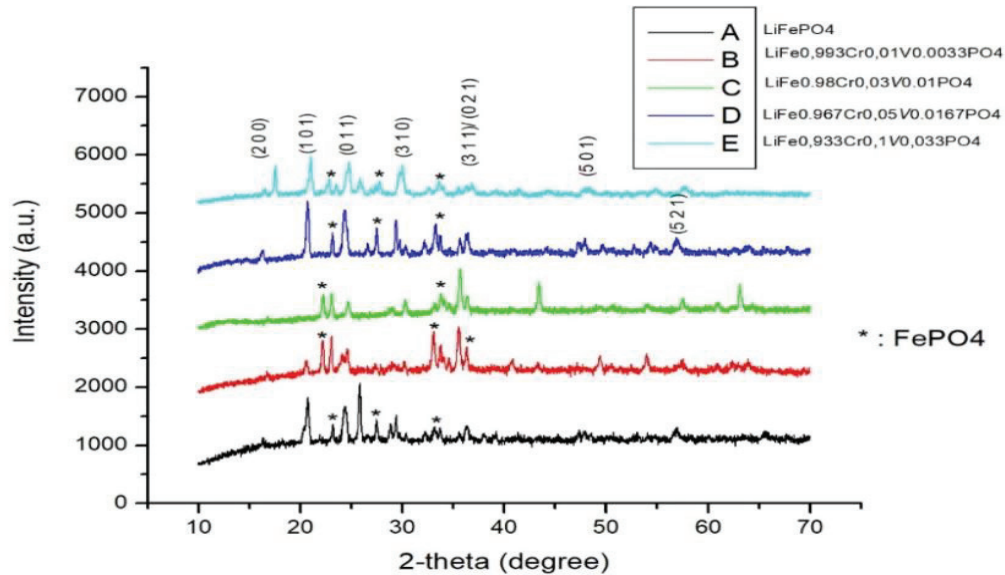
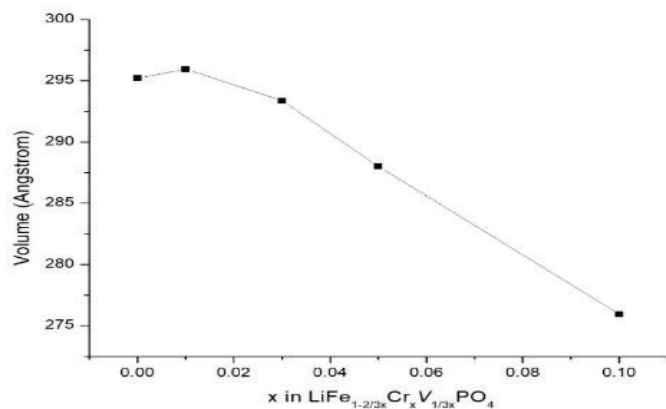


FIGURE 2. XRD Diffraction Pattern of  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$

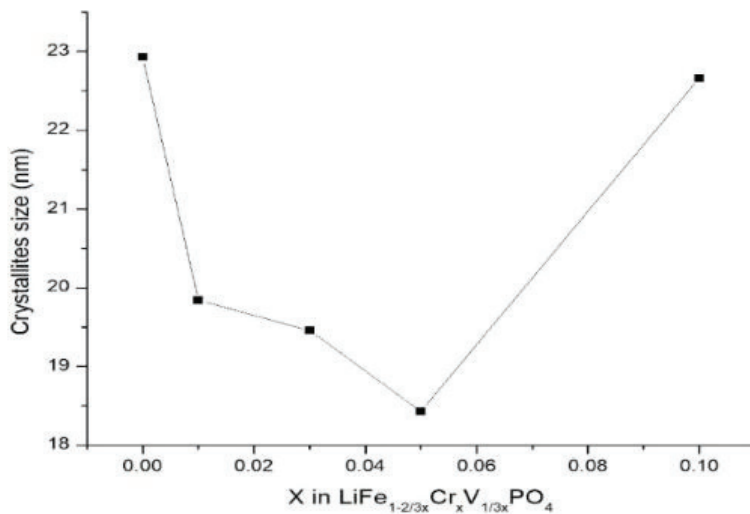
Other indicated phases in the experiment include  $\text{FePO}_4$  and  $\text{Cr}_2\text{O}_3$ . In the formation of  $\text{LiFePO}_4$  crystals using the solvothermal-microwave irradiation method, another  $\text{LiPO}_4$  phase is formed due to lack of  $\text{Fe}^{2+}$  precursors, and as a result,  $\text{LiFePO}_4$  crystals are not formed [12]. Those phases are not identified as  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  absorption. In addition, there is absorption in compounds with no Cr doping. There is a possibility that the by-product is the  $\text{FePO}_4$  compound since the most considerable characteristics seen are similar [13].

Based on the analysis using the U-Fit program, doping addition associates with the lattice parameters of the synthesized compound. The more the addition of the doping mole variation, the smaller the volume of the crystal cell. The crystal cell volume does not significantly decrease due to a relatively limited variety of precursor moles. Crystal volume decreased due to replacement of the Fe site by the Cr site. The ionic radius of  $\text{Cr}^{3+}$  is 62 pm and the radius of  $\text{Fe}^{2+}$  is 78 pm so that the more Cr the replacement at the Fe site, the crystal volume will decrease.



**FIGURE 3.** Relationship between mol ratio and crystal volume in  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$

Based on the analysis of crystal size using the Debye-Scherer method, as the x value increases, the crystal size tends to decrease. As the x value increases, the crystal size decreases. This is because the increasing value of x, the more Cr atoms are added. This is closely related to the radius of the Cr ion which is smaller than the Fe ion, so that the crystal size decreases with increasing x value. This is also influenced by the crystallinity of XRD result data which is quite low so that it affects the crystal size calculation results



**FIGURE 4.** Relationship between mol ratio and particle size (nm) in  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$





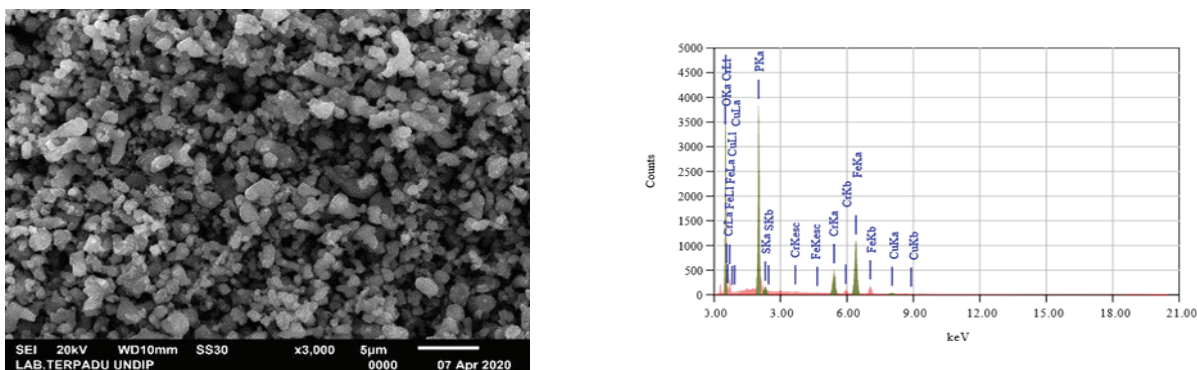


FIGURE 7. SEM and EDX of  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$

The results of SEM-EDX analysis show that the surfaces of  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$  compounds are hollow and irregular in shape. The ratio of Fe:P:O mole from  $\text{LiFePO}_4$  compound is 1:1:8, while the ratio of Fe: Cr: P: O mole of  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$  compound is 0.77: 0.23: 1:7. This is probably due to the formation of other phases such as  $\text{Cr}_2\text{O}_3$  and Fe elements which are bound to form intermediate compounds such as  $\text{FePO}_4$ ,  $\text{Fe}_2(\text{PO}_4)_3$  and  $\text{LiFeHPO}_4$  so that the ratio of O atoms tends to increase compared to theory.

## CONCLUSION

Based on the research and data analysis conducted, it is concluded that  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  compounds ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) can be synthesized using solvothermal-microwave irradiation method. The XRD data analysis results show that the  $\text{LiFe}_{1-2/3x}\text{Cr}_x\text{V}_{1/3x}\text{PO}_4$  ( $x = 0; 0.01; 0.03; 0.05; 0.1$ ) has a *Pnma* space group with lattice parameters in the range  $a = 10.36\text{-}10.13 \text{ \AA}$ ,  $b = 6.08\text{-}5.53 \text{ \AA}$ ,  $c = 4.74\text{-}4.93 \text{ \AA}$ , and crystal volume in the range  $302.7\text{-}275.94 \text{ \AA}^3$ . The increasing value of added mol  $x$  further increases the value of the lattice parameter. The XPS result revealed that the oxidation states of Fe, P, O and Cr in  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$  were found to be  $2+/3+$ ,  $5+$ ,  $2+$  and  $3+$ , respectively. SEM-EDX analysis shows that the surfaces of  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.967}\text{Cr}_{0.05}\text{V}_{0.0167}\text{PO}_4$  compounds are hollow and irregular in shape. Increasing the value of the  $x$  mol ratio causes the crystal size to decrease

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