Synthesis and Characterization of LiFePO₄ By Variation Addition Of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ as Cathode Material For All-Solid-State Li-ion Battery

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Abstract. The safety of lithium-ion batteries have always been a concerned for industrial application. Therefore, there is a strong interest to produce an all-solid-state battery. An all-solid-state battery has several advantages, including easy fabrication, non-flammable, low leakage, but mainly because it is safer. In this study, (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ was synthesized as solid electrolyte. Meanwhile, as cathode, LiFePO₄ was added by variations of: 0%, 10%, and 30% of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ to minimize the presence of solid state interface between solid electrolyte and cathode. The samples were characterized using Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and conductivity measurement. For SEM images, the particle distribution was not thoroughly homogeneous because it was prepared manually by only grinding the samples. The X-ray data showed that (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ has halo pattern and the crystal structure of synthesized cathode belongs to Pmna space group (Olivine Structure). The range of measured AC conductivity was around 10⁻⁴ S/cm - 10⁻⁸ S/cm.

Keywords: Lithium-ion battery, LiFePO₄, (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅, Solid Electrolyte

1. Introduction
A rechargeable battery plays a significant role to provide an efficient storage of electrical energy as chemical energy [1]. There are numerous types of rechargeable batteries, including rechargeable Li-ion batteries (LIBs). LIBs have several advantages, such as, long life cycle, high power density, low self-discharge property, high gravimetric, and volumetric energy [2-8]. Currently, the major cathode materials being explored are LiMn₂O₄, LiNiO₂, LiCoO₂, and their composites [1, 10-12]. Unfortunately, LiMn₂O₄ is struggling with cycling and thermal stability and pure LiNiO₂ is isothermal and cannot commercialize due to safety concerns. Even though, LiCoO₂ has been widely commercialized, there are safety concerns considering LiCoO₂ is toxic and very expensive [13].

On the other side, LiFePO₄ is a good choice to be a cathode material for Li-ion batteries, safer charging/discharging, good theoretical capacity at 170mAh/g and a flat voltage of 3.4 V. But the
major drawback of LiFePO₄ is its much lower electronic conductivity (10⁻⁹ S.cm⁻¹) compared to other cathode, such as, LiCoO₂ (10⁻⁵ S.cm⁻¹) [14]. However, the increasing number of fire incidents in electrical vehicles and in airplanes is a huge concern for Li-ion batteries. One way to improve the safety and improving the lifecycle of the batteries is to replace the liquid electrolytes by solid electrolytes to avoid the grow of dendrite formation [15-17]. Even though, liquid electrolytes have a high ionic conductivity (12 mS/cm for 1 M LiPF₆ in EC-DMC at 27°C) but it is risky because its being flammable [18].

A previous work on solid electrolyte was performed by E.Kartini et al. [19-20] on Li₃PO₄ and LiPO₃. Furthermore, T.Utomo [21] using (Li₃PO₄)₅(AgI)₃(LiI)₂ as percursor. The reason why Li₃PO₄, AgI, LiI, are chosen to be solid electrolyte because of several reasons. Li₃PO₄ has been proved to be a good candidate for solid electrolyte, due to its easy in preparation, high melting temperature, low cost, and good compatibility with the electrode materials [22]. While AgI and LiI as dopants can increase the electrical conductivity of Li₃PO₄ [23]. The focus on the previous work was on synthesis and characterization of molar ratio between x:y:z to make the perfect solid electrolyte. The molar ratio which used was vary from 1:0:0 to 0.34:0.33:0.33. However, the optimum conductivity was achieved for the composition of 0.5:0.25:0.25 or (Li₃PO₄)₀.₃(AgI)₀.₂₅(LiI)₀.₂₅ namely 8.3349x10⁻⁵ S/cm and the rest were around 10⁻⁵ S/cm and 10⁻⁶ S/cm. The X-ray diffraction data shows that all samples have similar crystal structure with different intensity due different compositions.

The main purpose of this study is to synthesis solid electrolyte from (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ and cathode material using LiFePO₄ by the addition of 0%, 10%, and 30% of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ in order to obtain cathode and solid electrolyte that is applicable for solid state battery. The addition of solid electrolyte to the cathode is to prevent the solid state interface between solid electrolyte and cathode. Further application, all-solid-state lithium-ion battery will be made from these cathode and solid electrolyte.

2. Experimental method

All of activities of synthesis and characterizations were carried out at the Integrated Battery Laboratory, Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency, Indonesia.

2.1 Sample preparation of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅

In this study, (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ has been prepared manually. The appropriate amounts of lithium phosphate, silver iodide, and lithium iodide with the molar ratio 0.5:0.25:0.25 were mixed inside of glove box. It was mixed manually by grinding on the agate mortar for approximately 45 minutes.

2.2 Sample preparation of LiFePO₄-(Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅

The solid electrolyte of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ has been made was added to LiFePO₄ by mixing and grinding them together using agate mortar inside of glove box for approximately 45 minutes. The appropriate amounts of lithium iron phosphate and solid electrolyte with the molar ratio 10:0, 9:1, and 7:3.

2.3 Characterization of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ and LiFePO₄-(Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅

The characterization of solid electrolyte of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ and cathode of LiFePO₄-(Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ were measured by XRD and SEM measurements. The purpose of XRD measurement is to see if solid electrolyte was successfully added to cathode and to find out the crystal structure of LiFePO₄-(Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅. The measurements were operated at 45 kV and 40mA, a can rang from 10° to 80° [29] that is conducted at room temperature by PANalytical Empyrean diffractometer equipped with PIXcel 1D detector SEM measurements were operated at 20kV, a chamber pressure of 20 Pa, wide distance of 10 mm and Spot Size of 65 using JEOL JSM-6510LA. The measurements were done to see the morphology of samples. AC Impedance
Measurement of samples were carried out using HIOKI LCR HiTester 3532-50 to see the electronic conductivity of each samples.

3. Results and discussion
The reason why all the preparations were done inside the glove box because lithium iodide is easily oxidized when it’s exposed to air. The observation of morphology analysis was obtained by scanning electron microscopy (SEM). All the entire images of SEM show the morphology that was obtained by backscattered electron. Backscattered electron determine the density difference of atom in samples. Atom which has bigger density will produce more bright than the atom which has a smaller density.

![Figure 1](image1.png)

**Figure 1.** The SEM micrograph of (a) Solid Electrolyte (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ (b) LiFePO₄-0% (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ (c) LiFePO₄-10% (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ (d) LiFePO₄-30% (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅

Figure 1 shows microstructures of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ and LiFePO₄ by variation addition of 0%, 10%, and 30% of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ are shown in Figure 1(a), 1(b), 1(c), and 1(d), respectively. All samples produced partially crystalline samples which consist of porous agglomerates. The agglomerates indicate the compound has particles smaller than the size shown in the micrograph. As shown in the Figure 1 that the samples were not thoroughly homogeneous throughout the sample due to the preparation by only manually grading using agate mortar estimated 45 minutes. Further increasing amount of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅, the sample crystallized with similar crystal structure since the addition of of (Li₃PO₄)₀.₅(AgI)₀.₂₅(LiI)₀.₂₅ was not significant.

The XRD characterization is used to identify if solid electrolyte (SE) of (Li₃PO₄)₀.₅(LiI)₀.₂₅(AgI)₀.₂₅
is added successfully into the cathode of LiFePO$_4$. The wavelength for x-ray diffraction is $\lambda_x \sim 1.54$ Å (from CuK$\alpha$ target) and for neutron $\lambda_n \sim 1.82$ Å (from Ge (331) monochromator).

Figure 2 shows the data characterization of samples of $(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$ and LiFePO$_4$-0% $(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$ before and after the addition of $(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$ with variations of 10% and 30%. As the figure shows can be concluded that the solid electrolyte was successfully added to LiFePO$_4$. From Figure 2(a), it shows that $(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$ has an amorphous phase. The X-ray diffraction data is showing only a halo pattern. The broad peak position at $2\theta \sim 23^\circ$ shows that the solid electrolyte mostly consists of $\text{Li}_3\text{PO}_4$ crystal. From Figure 2(b), it shows that the whole peaks of diffraction were proper to the standard LiFePO$_4$ indexed to olivine structure, orthorhombic space group $Pnma$ (JCPDS No.083-2092). The strong and sharp peaks show that the LiFePO$_4$ sample was very crystalline. Figure 2(c) and Figure 2(d) show the crystal structure after the addition of 10% and 30% of $(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$. The broad peak position at $2\theta \sim 23^\circ$ shows that the solid electrolyte was successfully added to LiFePO$_4$. The figures also show different peaks and different intensity. Different peaks show that peaks caused by the addition of solid electrolyte and different intensity of peaks caused by the amount of the addition. But, more detail is still needed.

One of the disadvantages of $\text{Li}_3\text{PO}_4$ as a solid electrolyte is the low conductivity which was the reason why AgI and LiI were added as dopants. AgI and LiI compounds are believed to increase the conductivity because they have crystal defects which play an important role in ion transport. Figure 3 shows the AC conductivity of samples, it can be seen that those with the highest AC range conductivity was LiFePO$_4$-10%$(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$. That was the reason why LiFePO$_4$-10%$(\text{Li}_3\text{PO}_4)_{0.5}(\text{LiI})_{0.25}(\text{AgI})_{0.25}$ will be chosen to be coated onto the aluminium foil.
Because it had higher range of AC conductivity compared to LiFePO$_4$-0\%(Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$ and LiFePO$_4$-30\%(Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$. But the challenge was that the conductivity was still in AC, which means it was frequency dependence. There were several reasons why it was still in AC range conductivity, including, the voltage used for the experiment was low.

The values of AC conductivity were vary from $10^{-8}$ S/cm to $10^{-4}$ S/cm in the frequency from 1 Hz to $10^6$ Hz. There was an increase for the LiFePO$_4$-10\%(Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$ shows that the optimum composition for cathode was by the addition of 10\%(Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$. This cathode is to be used for further application in all-solid-state battery.

4. Conclusion

The sythesis of solid electrolyte (Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$ by molar ratio of 0.5:0.25:0.25 and cathode LiFePO$_4$ with variation of 0\%, 10\%, 30\% of solid electrolyte (Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$ by molar ratio of 10:0, 9:1, and 7:3 were successfully prepared manually by grinding each of the LiFePO$_4$, Li$_3$PO$_4$, AgI, and LiI materials inside of the glove box. SEM images of samples show that the samples were not homogeneous thoroughly throughout the sample, possibly because it was prepared manually. XRD measurement data is used to see the success of adding solid electrolyte to the cathode LiFePO$_4$, this has been proved by the presence of peaks after the addition of solid electrolyte mostly peaks of Li$_3$PO$_4$. The intensity of the peaks are changed with the increasing amount of solid electrolyte on the cathode LiFePO$_4$. The impedance measurement was used to calculate the conductivity of each material, and it was found that the highest conductivity was obtained LiFePO$_4$-10\%(Li$_3$PO$_4$)$_{0.5}$LiI$_{0.25}$AgI$_{0.25}$. This study gives the idea of all-solid-battery preparation and how to reduce the presence of solid electrolyte interface problem.

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