Synthesize & Characterization of Li₃PO₄(0.5)LiI(0.25)LiCl(0.25) Solid Electrolyte for Lithium Ion Battery

Gde Paksi Raganata1*, Evvy Kartini1**, Heri Jodi2, Wahyudianingsih2, Agus Sudjatno2, and Philips Nicolas Gunawidjaja1

1Department of Physics, Faculty of Information Technology and Sciences, University of Parahyangan, Jl. Ciumbuleuit No. 94, Kota Bandung 40141, Indonesia
2National Agency of Nuclear Energy, Jl. Kawasan Puspiptek, Kota Tangerang Selatan 15310, Indonesia

* paksiraganatag@gmail.com ; ** kartini@batan.go.id

Abstract. Lithium phosphate (Li₃PO₄) is a promising candidate for solid electrolytes. However its ionic conductivity still stands at 3 × 10⁻⁷ S/cm which is very low compared to liquid electrolytes which are contained within widely distributed lithium ion batteries at 10⁻³ S/cm. This requires a solution to increase its conductivity which is the addition of dopants. The proposed dopants are lithium iodide (LiI) and lithium chloride (LiCl) which is mixed with the Li₃PO₄, creating the new solid electrolyte system Li₃PO₄(0.5)LiI(0.25)LiCl(0.25). The mixture had an ionic conductivity of 8 × 10⁻⁴ S/cm observed through electrochemical impedance spectroscopy (EIS). The crystal structure observation using x-ray diffraction identified the Li₃PO₄ belongs to the Hermann-Mauguin symmetrical space group of Pmnb.

Keywords: Li₃PO₄, LiI, LiCl, solid electrolyte, ionic conductivity

1. Introduction

Solid electrolytes have been developed extensively as an alternative to liquid electrolytes. The liquid ones are deemed more risk because of the flammability of most of its materials [1]. Aside of that, due to the oxidation happening inside the liquid electrolytes which results in the batteries itself expanding. This may cause the internal structure of liquid batteries to change, resulting in electrolyte moving through the separator which may cause short circuit from connection between Anode and Cathode [2]. Lithium phosphate (Li₃PO₄) is a promising network former for solid electrolytes as reported by Evvy et al in 2016 which was created by mixing lithium hydroxide (LiOH) and phosphoric acid (H₃PO₄) via wet chemical reaction and lithium oxide (Li₂O) and phosphorus pentoxide (P₂O₅) via solid state reaction (melt-quenching) [3-5]. The highest ionic conductivity obtained through the study was via solid state reaction which measured was measured at 3 × 10⁻⁷ S/cm.

The meager ionic conductivity requires an additive to exceed the ionic conductivity of liquid electrolytes which measures at 10⁻³ S/cm [6] hence the addition of dopant salts. These salts increase ionic conductivity of network formers by enriching the lithium content in which they only react statically inside the electrolyte [7]. Examples of dopants include lithium iodide (LiI), silver iodide (AgI), lithium chloride (LiCl), and silver chloride (AgCl). Research about dopants have been conducted extensively throughout the years. Makhson et al in 2012 added AgI and LiI which increased the conductivity of
AgPO$_3$ to 10$^{-2}$ S/cm [8]. Kaus et al in 2009 added LiI into Li$_3$PO$_4$ which increased its conductivity to 10$^{-3}$ S/cm and also did it with several concentration which gave its optimal at 45-50 % [9]. Other experiments also include the work of Tanaka et al in in 1988 about the production of LiCl + Li$_2$O + TeO$_2$ glass which has an ionic conductivity of 10$^{-6}$ S/cm [10] and the work of Kharbachi et al in 2020 about the LiBH$_4$-LiCl-P$_2$S$_5$ system which with an ionic conductivity measured at 10$^{-3}$ S/cm [11].

In this research, two dopants are chosen which are LiI and LiCl. The wide usage of these materials influenced its selection for the experiment. Their ionic conductivities measured respectively at 10$^{-7}$ S/cm and 10$^{-6}$ S/cm [12, 13]. The material is a mixture of Li$_3$PO$_4$ which was the product of solid state reaction from the research of Nur et al [4], LiI, and LiCl with a molar ratio of 2:1:1 which will be labeled Li$_3$PO$_4$(0.5)LiI$_{0.25}$LiCl$_{0.25}$. The material is created via wet chemical reaction which is grinding using mortar and pestle. Properties of the materials are also examined to be used as comparison between other researches. Electrical property will be measured using electrochemical impedance spectroscopy (EIS) [14] and the crystal structure will be observed using x-ray diffraction (XRD) [15]. The addition of these dopants is expected to increase the base conductivity of Li$_3$PO$_4$ from 3 × 10$^{-7}$ S/cm to compete with or even exceed those of liquid electrolytes.

2. Experimental method

2.1. Experimental Diagram

![Figure 1. The flow chart of experimental diagram of the research.](image1)

![Figure 2. The Li$_3$PO$_4$(0.5)LiI$_{0.25}$LiCl$_{0.25}$ mixture in the form of powder.](image2)

The experiment is first done by mixing all the ingredients into one homogenous powder (all three components are in powder form). The raw materials used are Li$_3$PO$_4$, LiI (MERCK), and LiCl (Sigma ALDRICH). In the sample preparation, the materials are weighed together according to the molar ratio of 2:1:1. The materials are then grinded using a mortar and pestle. For the electrochemical impedance spectroscopy (EIS), the materials must be shaped into an easily measured symmetrical form hence the forming of pellet using a portion of the mixture. The remaining powder is then used for characterization using x-ray diffraction (XRD).
### 2.2. Sample preparation

The materials (Li₃PO₄, LiI, and LiCl) in the form of powder are first weighed using a digital scale according to its molar ratio. A total of 30 g of material is used. Using the relation between mass ratio and molar ratio, the mass of each component within the mixture can be determined, via equation (1).

\[
\omega_i = x_i \frac{M_i}{\sum_j x_j M_j}
\]  

(1)

With \(\omega_i\) being the mass ratio, \(x_i\) the molar ratio of the weighed component, \(M_i\) the molar mass of the component in g/mol, and \(\sum_j x_j M_j\) as the sum of the molar mass of all the components multiplied by its molar ratio.

| Component | Mass (g) |
|-----------|----------|
| Li₃PO₄    | 17.03    |
| LiI       | 9.84     |
| LiCl      | 3.11     |

The whole mixture is then grinded together for four hours using a mortar and pestle in room temperature until it becomes homogenous. After the mixing, the sample is placed within a porcelain crucible and dried frequently using an oven at 50°C in between processes to remove water particles (due to LiI and LiCl being highly hygroscopic).

### 2.3. Pellet Forming

For the EIS, the sample must be shaped into small cylindrical pellets. The process is done by putting the powder into a mold. The mold is then pressed vertically using a hydraulic presser. After the pressing, the pellet is then re-dried in the oven.

### 2.4. Electrochemical Impedance Spectroscopy (EIS)

The pellets are then measured to obtain its diameter and thickness and Ag paste is applied on it. The test uses a HIOKI 3532-50 LCR HiTESTER LCR meter and is run through a measuring frequency of 5 Hz to 5,000,000 Hz. During the LCR test, the pellet is placed between two electrodes and a plot of its conductance is obtained. Using the formula in equation (2) of conductivity, its ionic conductivity can be obtained which is as follows:

\[
\sigma = G \left( \frac{h}{A} \right)
\]  

(2)

where \(\sigma\) is the conductivity in S/cm, \(G\) is the conductance in S, \(h\) is the thickness of the pellet in cm, and \(A\) is the surface area of the pellet in cm². The result is then plotted into two graphs. The first graph is the Cole-Cole plot to observe its impedance, and the second is the conductivity to measuring frequency graph. The conductivity graph is put into logarithmic scale to observe the obtain its conductivity according to the Jonscher Power Law:

\[
\sigma_{total} = \sigma_{DC} + A \omega^n
\]  

(3)

Where \(\sigma_{total}\) is the total conductivity in S/cm, \(\sigma_{DC}\) is the DC conductivity, and \(A\omega^n\) is the AC conductivity with \(n\) being the power constant (0 < \(n\) < 1).
2.5. X-Ray Diffraction (XRD)
The XRD characterization in this experiment uses a Malvern Panalytical Type Empyrean diffractometer. The peaks are observed from a 2θ value of 10° to 80°. The peak values from this test would then be processed using Rietveld refinement to discover its new lattice information. The peaks would then be plotted into intensity to 2θ graph.

3. Results and discussion

3.1. Electrochemical Impedance Spectroscopy (EIS)

Table 2. Impedance and DC conductivity value of Li$_3$PO$_4$(0.5)LiI(0.25)LiCl(0.25) mixture.

| R (Ω) | σ (S/cm) |
|-------|-----------|
| 4.83  | 8 × 10$^{-4}$ |

The EIS test shows that the Li$_3$PO$_4$(0.5)LiI(0.25)LiCl(0.25) mixture had an ionic conductivity in the value of $8 \times 10^{-4}$ S/cm. Compared to the ionic conductivity of the Li$_3$PO$_4$ created by Evvy et al. [3], which had an ionic conductivity of $3 \times 10^{-7}$ S/cm, the addition of dopants have increased the conductivity by several orders. The conductivity however still stands lower compared to the works of Kaus et al and Makhsun et al which electrolyte systems are able to reach $10^{-3}$ S/cm or even $10^{-2}$ S/cm which even exceeds those of liquid electrolytes. The work of Makhsun et al [8] however involves the process of melt quenching which is heating the material to achieve a more amorphous structure first, hence the higher conductivity.

3.2. X-Ray Diffraction (XRD)
The crystal structure observation which uses XRD and is analyzed using Rietveld refinement gave the information of the crystal structures of each of the components. The Li$_3$PO$_4$ used belonged to the Hermann-Mauguinn symmetry space group P m n b [16], the LiI belonged to the F m -3 m space group [17], and the LiCl also belonged to the F m -3 m space group [17]. The crystal structure of Li$_3$PO$_4$ made by Evvy et al using solid state reaction also belonged to the P m n b space group which means its structure remain unchanged because the materials are only mixed as a composite. The lattice parameters for the Li$_3$PO$_4$ are a = 4.8600 Å, b = 6.0700 Å, and c = 10.2599 Å, for LiI are a = 10.3415 Å, b = 5.5693 Å, c = 6.6374 Å, and for LiCl are a = 3.8300 Å, b = 3.8300 Å, and c = 3.8300 Å.
### Table 3. Rietveld refinement result of the Li₃PO₄(0.5)LiI(0.25)LiCl(0.25) mixture.

| Formula | Li₃PO₄ | LiI | LiCl |
|---------|--------|-----|------|
| Lattice Parameters | P m n b | F m -3 m | F m -3 m |
| a (Å) | 4.8600 | 10.3415 | 3.8300 |
| b (Å) | 6.0700 | 5.593 | 3.8300 |
| c (Å) | 10.2599 | 6.6374 | 3.8300 |
| α (°) | 90 | 90 | 90 |
| β (°) | 90 | 90 | 90 |
| γ (°) | 90 | 90 | 90 |
| R<sub>exp</sub> (%) | 4.75 | 4.75 | 4.76 |
| R<sub>wp</sub> (%) | 95.7 | 94.2 | 98.9 |
| X<sup>2</sup> | 405 | 392 | 432 |

### 4. Conclusion

Based on the results of the experiment, it is concluded that the addition of LiI and LiCl as dopants for the Li₃PO₄ solid electrolyte did increase its ionic conductivity. The Li₃PO₄(0.5)LiI(0.25)LiCl(0.25) system achieved an ionic conductivity of $8 \times 10^{-4}$ S/cm, which is close to that of liquid electrolytes conductivity which stands at $10^{-3}$ S/cm. This value has been increasing about three orders of magnitudes from the Li₃PO₄ ionic conductivity which stands at $3 \times 10^{-7}$ S/cm. The crystal structure observation revealed that the Li₃PO₄ still belongs to the same space group of P m n b as reported by Evvy et al.[5] due to only
being mixed together with the dopants as a composite. For further research, it is suggested to make the composite with different concentration which can be related to changes in ionic conductivity and to and to find the optimal portion of dopants within Li$_3$PO$_4$.

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