The influence of chitosan concentration on morphology and conductivity of lithium aluminium titanate phosphate for solid electrolytes of lithium-ion battery application

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Abstract. Nowadays, Lithium-Ion Battery (LIB) is considered as one of the most popular energy storage technologies due to their superior properties such as light-weight and high energy density. However, LIB technologies still lack of safety problem because utilization of liquid electrolytes may drive to explosion at high temperature. Thus, development of solid electrolytes based on lithium aluminium titanate phosphate (LATP) have attracted a lot of attention because they are safer than liquid electrolytes. However, utilization of LATP as solid electrolytes in LIB still limited because of their conductivity is lower than liquid electrolytes. Porous LATP are expected to solve this low conductivity problem by increasing their surface area and their ability to deliver ion. In this research, porous LATP were synthesized using sol gel method and chitosan as template. Concentration of chitosan were varied from 0.0–2.0% w/v to know the influence of chitosan to morphology and properties of obtained LATP. Based on X-ray Diffraction (XRD), all of samples contained LiTi2(PO4)3 (JCPDS PDF 35-0754) and AlPO4 (JCPDS PDF 11-0500), which are part of LATP. Based on Brunauer-Ernett-Teller (BET), Scanning Electron Microscope (SEM), and Electron Impedance Spectroscopy (EIS) analysis, 0.5% w/v chitosan concentration is the optimum condition to obtain the highest surface area (10.7 m²/g) and ionic conductivity (2.2x10⁻⁷ S/cm).

Keywords: chitosan, lithium-ion battery, porous LATP, solid electrolytes, sol gel method

1. Introduction

Nowadays, Lithium-ion Battery (LiB) is considered as one of the most popular energy storage technologies due to their superior properties such as light-weight, high energy density and long cycle life [1-6]. However, current LiB technology are not safe enough because of utilization of liquid electrolytes that are flammable, lead to fire or even explosion. In this context, development of all-solid state LiBs, particularly solid electrolytes as replacement of liquid electrolytes, is attractive in term of safety and stability [3-9]. Various crystal structures of ceramics such as Li3N [10], garnet-type doped Li2La2ZrO12 [11], and NASICON-type LiMe2(PO4)3 (M=Ti, Ge, Hf, Zr, Sn) [3-9] have been studied as potential solid electrolytes for all-solid state LiBs. Among them, Lithium Aluminium Titanate Phosphate (LATP) with NASICON-type structure is considered as the most promising candidates for solid-state electrolytes due to their high conductivity (up to 7.0x10⁻⁴ S/cm) [9] and high air-stability at room temperature [3-9]. Also, mass production of LATP can be prepared by simple co-precipitation.
method without inert atmosphere [7]. Nevertheless, exploitation of LATP in LiB technology still limited because of their ionic conductivity is not enough for high-rate LIBs application (>10^{-2} S/cm) [3]. Therefore, an effort to improve ionic conductivity of LATP is important to achieve a safer LiB technology.

Preparation of nanosized LATP may answer this challenge because distance for lithium-ion transport is decreased at smaller particle size, lead to increasing the rate of lithium mobility in solid electrolytes [1, 2]. Also, nano-sized particles provide better electron transport and higher surface area for better contact between electrolytes and electrode [1, 2]. However, preparation of nano-sized particles is quite difficult because nano-sized particles tend to agglomerate to form bigger particles. Several methods have been used to prepare nanosized particles such as sol gel method [9, 12], heterocoagulation [13], and microfluidic [14]. One of attractive method to prepare nano-sized particles is combining sol gel method with natural based-compound or materials as support or chelating agent because it can promote nucleation of monodispersed nanoparticles while preventing further agglomeration of nanoparticles [15]. Previously, we have been successfully prepared smaller particles size of fenton catalyst using bacterial cellulose as catalyst support [16] and LiMnO_{4} using chitosan as its chelating agent [17]. In this report, smaller particles size of LATP have been prepared by sol gel method combined with chitosan as chelating agent. Chitosan concentration has been varied to know the influence of chitosan concentration to morphology and properties of obtained LATP.

2. Materials and Methods
LiNO_{3}, H_{2}O, Al(NO_{3})_{3}, 9H_{2}O, TiCl_{4}, and (NH_{4})_{2}HPO_{4} that used in this experiment are pro analyst (p.a) grade and were purchased from sigma Aldrich. Chitosan with molecular weight of 231,736 g/mol (determined by viscometry method) was purchased from CV. Biochitosan Indonesia. LATP were prepared by co-precipitation sol gel method [7]. All of LATP precursor with concentration 0.1 M were mixed together, followed by gentle mixing with chitosan in 2% acetic acid solution at various concentration (0.0, 0.5, 1.0, and 2.0% w/v). Then, pH of solution was gradually increased by addition of ammonium hydroxide solution until pH solution reach 6 to form colloid phase. To reduce particles size and sustain their homogeneous dispersion, solution was mixed using ultrasonic homogenizer for 15 minutes. Powder of products were obtained by heating the solution at 100°C for about 24 hours to remove water content, followed by calcination process at 1000°C for 2 hours.

Obtained products have been characterized using several methods: (i) X-Ray Diffraction (XRD, Phillips Analytical X-Ray PW1835) to know all of crystal structure, (ii) Scanning Electron Microscope (SEM, JEOL-JSM-6510LV) to observed morphologies of obtained samples, (iii) Brunauer-Emmett-Teller (BET) was performed to reveal surface area, and (iv) Electrochemical Impedance Spectroscopy (EIS, GamryRef 3000) method was used to determine ionic conductivity.

3. Results and Discussions
XRD patterns of each sample can be seen in figure 1. In general, all of XRD pattern of obtained samples showed the presence of LiTi_{2}(PO_{4})_{3} and AlPO_{4}, which are generally found in the formation of LATP, and LiTiPO_{4}. Formation of two allotrope compounds, LiTiPO_{4} and LiTi_{2}(PO_{4})_{3}, might be occurred due to difference of exposing oxygen between inner and surface part of particles during calcination process. Surface part of particles were exposed with oxygen better than inner part of particles. As the consequences, there are possibility that LiTi_{2}(PO_{4})_{3} might be formed in the surface of particles and LiTiPO_{4} might be formed in the inner part of particles.
Even though LiTiPO$_5$ is an allotrope compound of LiTi$_2$(PO$_4$)$_3$, but their electronic state is different. Based on the electronic density of states (DOS), theoretical band gap of the ideal LiTiPO$_5$ (2.94 eV) is higher than the ideal LiTi$_2$(PO$_4$)$_3$ (2.38 eV) [18]. Thus, it was expected that electron mobility of LiTiPO$_5$ is slightly lower than LiTi$_2$(PO$_4$)$_3$. As can be seen in figure 1, samples with chitosan have higher amount of LiTiPO$_5$ than sample without chitosan. Therefore, it was expected that ionic conductivity of samples with chitosan is slightly lower than sample without chitosan.

However, conductivity of samples might not only depend on composition of crystal structure in sample, but also depend on their morphology and particle size. Thus, morphology of samples was observed by SEM method. SEM images of sample were presented in figure 2 and calculated particles size from SEM images can be seen in table 1. SEM observation revealed that sample prepared by sol gel method without addition of chitosan (figure 2.a) consisted of a mixture between small and big particles with average particles size 0.4±0.3 μm. While more uniform particles with average particles size 0.4±0.1 μm were observed on sample with 0.5% chitosan (figure 2.b). Increasing chitosan concentration to 1.0% (figure 2.c) and 2.0% (figure 2.d) lead to formation of big particles with average particles size 2.4±1.8 μm and 0.6±0.5 μm respectively. Considering that lithium mobility increase as particles size decrease [1, 2], it is expected that ionic conductivity of samples with 0.0% and 0.5% of chitosan might be higher than sample with 1.0% and 2.0% of chitosan.

**Figure 1.** XRD patterns of samples as a function of chitosan concentration.
Figure 2. SEM images of samples prepared with a) 0.0%, b) 0.5%, c) 1.0% and d) 2.0% of chitosan (scale bar represent 1 μm).

To know the influence of chitosan concentration to ionic conductivity of LATP, conductivity of samples was measured using EIS method. Representative of EIS curve in nyquist plot can be seen in figure 3, and summary of EIS data is presented in table 1. Conductivity measurement results revealed that sample with 0.5% of chitosan has the highest conductivity (24.0×10^{-7} S/cm) and sample with 1.0% of chitosan has the lowest conductivity (1.5×10^{-7} S/cm). Even though particles size of sample with 0.0% and 0.5% of chitosan are similar, but their conductivity is different. This phenomenon can be occurred because surface area of sample with 0.5% of chitosan (10.67 m²/g) is higher than sample without chitosan (3.91 m²/g), lead to higher ionic mobility and better contact between electrode and electrolytes in sample with 0.5% of chitosan [19]. During calcination process at 1000°C, chitosan in sample might disappear due to thermal degradation process of chitosan that might occurred at 280°C, lead to formation of sample with higher surface area [17, 20]. Meanwhile, lower conductivity was observed at sample with 1.0% (1.5×10^{-7} S/cm) and 2.0% of chitosan (2.2×10^{-7} S/cm) because of their bigger particles size and lower surface area.

Figure 3. EIS result with nyquist plot of sample with 0.0% chitosan as representative of EIS result.
Table 1. Summary of particles sizes of samples obtained from SEM results, surface area of samples obtained from BET results and conductivity obtained from EIS results.

| [chitosan] (% w/v) | Particle sizes (μm) | Surface area (m²/g) | Conductivity (× 10⁻⁷ S/cm) |
|--------------------|---------------------|---------------------|-----------------------------|
| 0.0                | 0.4±0.3             | 3.91                | 5.9                         |
| 0.5                | 0.4±0.1             | 10.67               | 24.0                        |
| 1.0                | 2.4±1.8             | 2.97                | 1.5                         |
| 2.0                | 0.6±0.5             | 2.42                | 2.2                         |

4. Conclusion
LATP have been successfully prepared using sol gel method combined with utilization of chitosan as chelating agent. Highest conductivity, smallest particles size and highest surface area of LATP sample can be achieved in this research with addition of 0.5% chitosan.

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