

Synthesis and characterization of PVA blended LiClO₄ as electrolyte material for battery Li-ion

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Abstract. It have been synthesized the materials for Li ion battery electrolytes, namely PVA with the addition of LiClO₄ salt were varied 0, 5, 10, 15 and 20% by weight respectively. The objective of this study is to control the ionic conductivity in traditional polymer electrolytes, to improve ionic conductivity with the addition of lithium perchlorat (LiClO₄). These electrolyte materials prepared by PVA powder was dissolved into distilled water and added LiClO₄ salt were varied. After drying the solution, PVA sheet blended LiClO₄ salt as electrolyte material for Li ion battery obtained. PVA blended LiClO₄ salt crystallite form was confirmed using X-Ray Diffraction (XRD) equipment. Observation of the morphology done by using Scanning Electron Microscope (SEM). While the electrical conductivity of the material is measured using LCR meter. The results of XRD pattern of LiClO₄ shows intense peaks at angles $2\theta = 23.2, 32.99, \text{ and } 36.58^\circ$, which represent the crystalline nature of the salt. Particles morphology of the sample revealed by scanning electron microscopy are irregular in shape and agglomerated, with mean size 200-300 nm. It can be concluded that polycrystalline particles are composed of large number of crystallites. The study of conductivity by using LCR meter shows that all the graphs represent the DC and AC conductivity phenomena.

1. Introduction

Safety concerns have limited the full utilization of lithium-ion batteries. Extensive efforts have been made to formulate an electrolyte that is nonflammable and still works well. It has been pointed out that there is a trade-off between an electrolyte's flammability and its performance in a cell. One strategy is to employ gelled polymer electrolytes as alternatives to the currently used organic carbonate electrolytes. The polymer electrolytes have high thermal stability, but their lithium-ion conductivity is low, either due to high viscosity or due to low mobility ion-conducting mechanisms. Another popular means is to add flame-retardants to increase thermal stability and to decrease flammability. The reported flame retardant additives include organicphosphates, phosphites, triazine, organic halogens, biphenyls, and a combination of halogens and phosphates [1].

All-solid-state cells using a solid electrolyte instead of a liquid electrolyte have safety advantages such as nonleakage and nonflammability [2]. An all-solid-state cell with sulfur itself as an active material could hardly be charged and discharged. An all-solid-state cell using sulfur-based materials as a positive



electrode and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramics or $\text{Li}_2\text{S}-\text{SiS}_2$ glasses as a solid electrolyte exhibited excellent cycling performance with a large capacity at room temperature [3].

Solid polymer electrolytes (SPE) show a lower ionic conductivity than the liquid electrolyte; however, they are less reactive with lithium, increasing the safety of battery. SPE, such as PEO-Li-salt complex, can be introduced to restrain the dissolution of polysulfides into the electrolyte. However, the linear PEO-Li-salt polymer electrolytes generally have some problems in lithium polymer battery. The problems are active reactivity of lithium anode at high temperature and low ionic conductivity at low temperature. Some researchers have tried to overcome the problems by the use of ceramic filler such as Al_2O_3 , SiO_2 , and TiO_2 in PEO based polymer electrolyte. It was reported that the additive improved the conductivity of PEO-base electrolytes as well as their interfacial resistance between the electrolyte and the lithium electrode. Moreover, the additions of ceramic fillers are accompanied with amorphous PEO structure. The amorphous PEO electrolyte also improves ionic conductivity [4].

Polymer electrolytes (PEs) are ionically conducting materials that may be used in the fabrication of solid-state electrochemical devices, particularly rechargeable batteries, electrochromic displays, capacitors and sensors. During the last decades different systems have been extensively studied and most of them were based on poly(ethylene oxide). More recently new types of electrolytes based on natural polymers (like cellulose derivatives, chitosan, starch or natural rubber) have been proposed due to their biodegradability, low production cost, good physical and chemical properties and good performance as SPEs (solvent-free polymer electrolytes) [5].

Several studies have been done in order to increase the conductivity of PVA. Kim et. al has studied PVA containing the salt lithium trifluoromethane sulfonate (LiCF_3SO_3 , LiTf) to overcome the low ionic conductivity PVA. It was found that the ionic conductivity of the PVA-based SPE increased with increasing salt concentration [6]. However, the relationship between the structure and properties of PVA based SPE is still needed to be explored.

In this study, we prepared PVA containing lithium perchlorat (LiClO_4) with various salt content to investigate the relationship between the bulk structure and electrical properties of SPE. The bulk structure is studied by scanning electron microscope (SEM) and X-ray diffraction (XRD). While the electrical properties is studied by electrochemical impedance spectroscopy (EIS). The objective of this study is to control the ionic conductivity in traditional polymer electrolytes, to improve ionic conductivity with the addition of lithium perchlorat (LiClO_4). This study is part of research material covering the battery anode, cathode and electrolyte materials in PSTBM, BATAN [7-10].

2. Materials and Methods

The powder of Poly Vinyl Alcohol, PVA (Aldrich, pro analysis, Germany) was dissolved into distilled water and added lithium chlorate salt LiClO_4 (Aldrich, pro analysis, Germany) were varied of 0, 5, 10, 15, and 20 % (w/w) respectively. After the drying process of the solution in an oven at a temperature of 70 °C, PVA sheet with addition of salt LiClO_4 obtained as an electrolyte materials for Li ion batteries. The PVA sheet with addition of LiClO_4 salt were then characterized by using X-Ray Diffraction (XRD, Shimadzu XD 610, Jepang), Scanning Electron Microscope (SEM, JEOL JSM 6510 LA, Jepang) and conductivity measurement by using LCR meter HIOKI 3532-50, China. The X-ray diffraction (XRD) measurement was carried out using a Cu $K\alpha$ radiation source ($\lambda=1.5406 \text{ \AA}$), with a step size of 4° min^{-1} from 5 to 90° .

3. Result and Discussion

PVA- LiClO_4 blended polymer electrolytes have been prepared by a solvent casting technique. XRD study revealed the occurrence of complexation between PVA and LiClO_4 in the composite matrix polymer. Figure 1 shows the XRD patterns of PVA with various weight ratio of LiClO_4 . The XRD pattern of LiClO_4 shows intense peaks at angles $2\theta \approx 20$, and 41° marked by bar sign in the Figure 1. The typical XRD pattern of PVA with 20 % LiClO_4 listed in Table 1 below shows intense peaks at angles $2\theta = 19.85$, 19.90 , 41.03 and 41.135° , which represent the crystalline nature of the salt. As shown in Figure 1b, 1c, and 1d, the XRD pattern of PVA with various LiClO_4 /PVA weight ratio show the incorporation of LiClO_4 into PVA decrease the crystallinity of PVA electrolyte. The calculated degree of crystallinity listed in Table 2. Figure 1 also shows the XRD patterns of Li-based PVA, most of the peaks pertaining to LiClO_4 disappeared in the Li-based PVA complexes, this indicates the complete dissolution of the LiClO_4 in the polymeric matrix. It is evident from Figure 1c and 1d that the amorphous nature is predominant in the Li-based PVA complexed system. It can be observed from the semi-crystalline peak of the PVA ($\theta \approx 20^\circ$) about the semi-crystal behavior of the PVA. The addition of LiClO_4 causes the decrease in the degree of the crystallinity and consequently the increase in the amorphicity of the material and its conductivity. The diffraction spectra of Li-based PVA showed the characteristic peaks of LiClO_4 predominantly, indicating that the crystal structure of LiClO_4 remained unaltered and no new phases were formed during the processing.

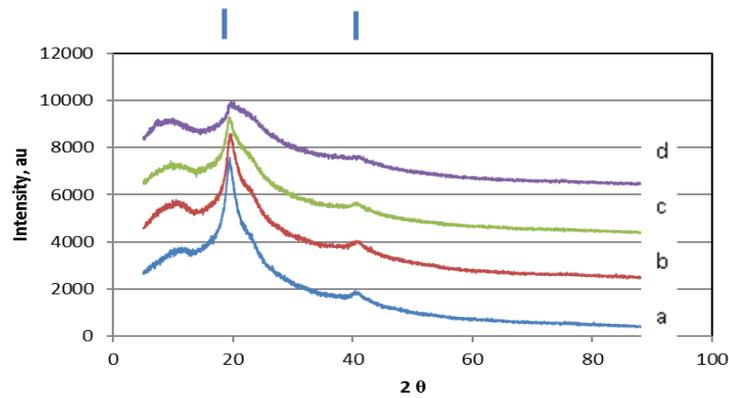


Figure 1. The XRD patterns of PVA with various weight ratio of LiClO₄, (a) 0% LiClO₄, (b) 5% LiClO₄, (c) 10 % LiClO₄ and (d) 20 % LiClO₄.

Figure 2a shows particle morphology of the sample revealed by SEM. The figure as seen is clear because there are no binder added yet. Meanwhile in Figure 2b, 2c and 2d correspond to the addition of LiClO₄ 5, 10 and 20 % into PVA matrix visible presence of particles in the matrix PVA. The particles are irregular in shape and agglomerated, with size about 200-1000 nm.

Table 1. The XRD pattern of PVA with 20 % LiClO₄.

| Pos. [°2Th.] | Height [cts] | Rel. Int. [%] |
|--------------|--------------|---------------|
| 19.8532 | 659.65 | 100.00 |
| 19.9030 | 329.83 | 50.00 |
| 41.0285 | 158.91 | 24.09 |
| 41.1350 | 79.46 | 12.05 |

Table 2. The calculated degree of crystallinity of composites prepared

| Weigth percent of LiClO ₄ in the PVA | degree of crystallinity % |
|---|---------------------------|
| 0 | 14.03 |
| 5 | 13.11 |
| 10 | 10.96 |
| 20 | 10.79 |

It can be concluded that polycrystalline particles are composed of large number of crystallites. Due to pronounced particle agglomeration, grain boundaries are not quite clear, and within a relatively broad grain size distribution. On the thin particle edges a thickness of several nanometers can be observed. We believe that this layer is responsible for improved electrical conductivity. As more pores appear, the

movement of electrons is resisted; and as the pore size increases, the charge-discharge efficiency decreases.

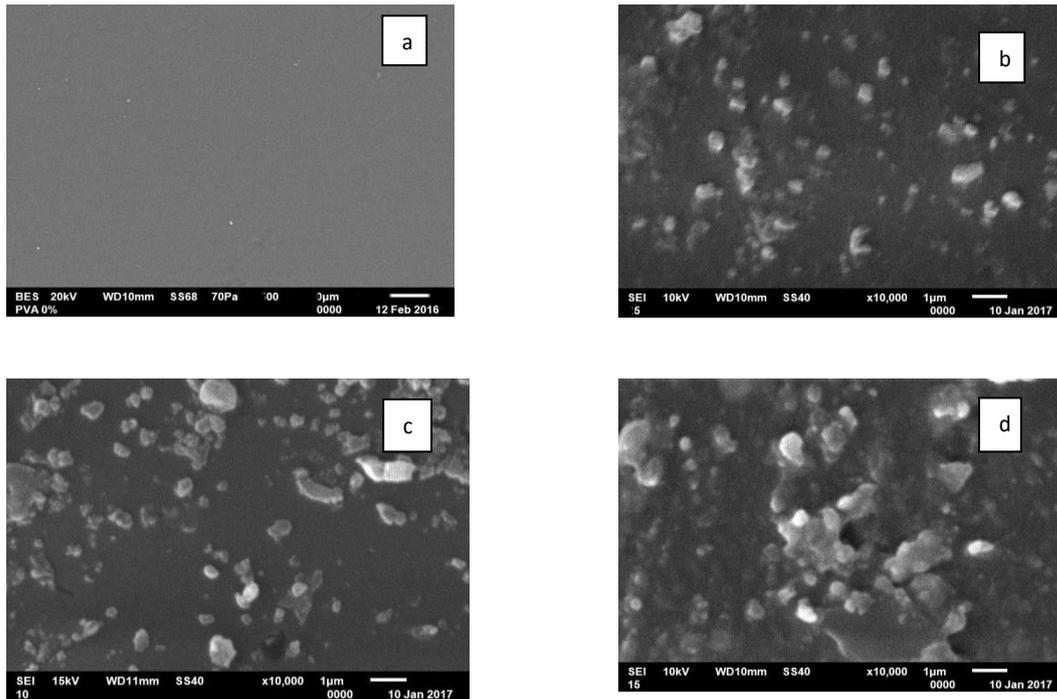


Figure 2. Morphology of the PVA–LiClO₄ blended polymer electrolytes at various weight ratio of LiClO₄, (a) 0% LiClO₄, (b) 5% LiClO₄, (c) 10 % LiClO₄ and (d) 20 % LiClO₄ revealed by scanning electron microscopy.

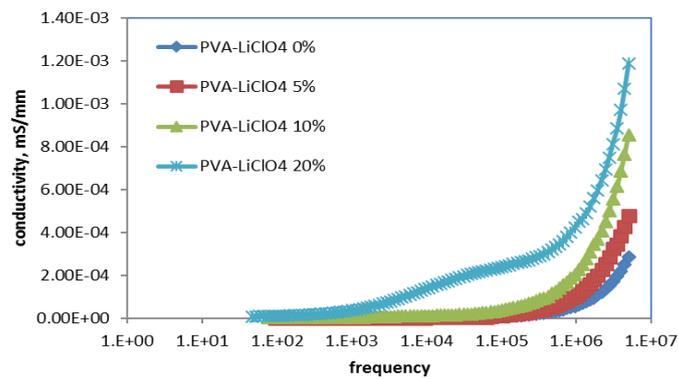


Figure 3. The electrical conductivity of PVA with various weight ratio of LiClO₄ as function of frequency.

The electrical conductivity of the electrolyte was calculated by equation, $\sigma = \lambda / (R_b XA)$ where R_b is the bulk resistance from AC impedance, λ the film thickness and A the surface area of electrode [11].

Figure 3 shows the electrical conductivity of PVA with various weight ratio of LiClO_4 . The conductivity of the material as a whole is a function of frequency, the graph shows the electrical conductivity of PVA with weight ratio of LiClO_4 0, 5, and 10 % have the same shape of straight lines at frequencies up to 800 kHz, and then increased with increasing frequency. At low frequencies up to 800 kHz the electrical conductivity is measured following the phenomenon of DC conductivity, and then increased with increasing frequency following the phenomenon of AC conductivity. DC conductivity is frequency independent conductivity typically assigned to the hopping conduction and AC conductivity has a power law behavior in terms of frequency. There are three effects that contribute to the AC conductivity: (i) electrode effects (active at low frequencies), (ii) DC plateau (at intermediate frequencies) and (iii) defect process [12]. The electrical conductivity of PVA with weight ratio of LiClO_4 20 % follow a straight lines at frequencies up to 1 kHz, makes a curve at frequencies up to 800 kHz, and then increased gradually with increasing frequency. Table 1 and Figure 4 show the electrical conductivity of PVA with various weight ratio of LiClO_4 measured at frequency of 750 kHz.

Table 3. The Electrical conductivity of PVA with various weight ratio of LiClO_4 measured at frequency of 750 kHz.

| LiClO_4 in the PVA (w%) | Electrical conductivity (750 kHz) mS/mm |
|----------------------------------|---|
| 0 | 9.48E-05 |
| 5 | 1.78E-04 |
| 10 | 1.86E-04 |
| 20 | 4.00E-04 |

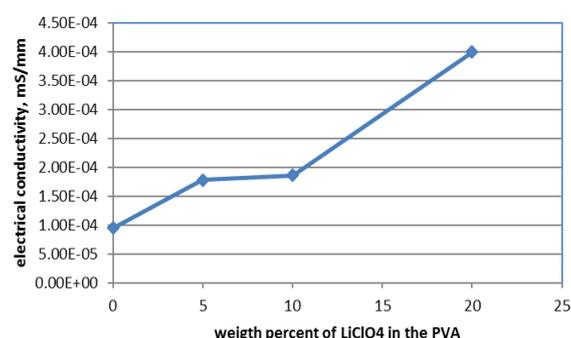


Figure 4. The electrical conductivity of PVA with various weight ratio of LiClO_4 measured at frequency of 750 kHz

It can be seen in Table 3 and Figure 4 that the effect of LiClO_4 addition into PVA tends to increase the conductivity of the material, especially in the addition of 0 to 5% and from 10 to 20%. Meanwhile, in addition of LiClO_4 as much as 5 to 10% the value of conductivity is almost the same. PVA is an insulating

material, with the addition of a conductive salt LiClO₄ it is clear that the more salt LiClO₄ added the conductivity of the composite increases.

4. Conclusion

The XRD patterns of Li-based PVA, most of the peaks pertaining to LiClO₄ disappeared in the Li-based PVA complexes, this indicates the complete dissolution of the LiClO₄ in the polymeric matrix. The diffraction spectra of Li-based PVA showed the characteristic peaks of LiClO₄ predominantly, indicating that the crystal structure of LiClO₄ remained unaltered and no new phases were formed during the processing. For next study suggested to conduct exploration on the addition of 15-20% LiClO₄. Particle morphology of Li-based PVA revealed by scanning electron microscopy showed the particles are irregular in shape and agglomerated, with size under micron. It can be concluded that polycrystalline particles are composed of large number of crystallites. The electrical conductivity of PVA with weight ratio of LiClO₄ 0, 5, 10 and 20% measured at frequency of 750 kHz are 9.48E-05, 1.78E-04, 1.86E-04 and 4.00E-04 mS/mm respectively.

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