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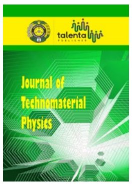

# Manufacture of Solid Polymer Electrolyte (SPE) Based on PVDF HFP-LiBOB

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**Abstract.** This research aimed to synthesize solid polymer electrolyte (SPE) with and without Polyethylene oxide (PEO) using the solution cast technique. The liquid electrolyte of LiBOB was synthesized with the immersing method. The chemicals used are PVDF-HFP (0.75 g), $TiO_2$(0.05 g), PEO(0.25 g), DMAC, EC, EMC, and LiBOB(1.55 g). The morphology of the surface membrane was characterized using SEM. The results of the SEM analysis shows that the addition of PEO plays a role in forming the SPE membrane because the addition of PEO greatly affects the density of the SPE sheet.

**Keywords:** conductivity, crystallinity, LiBOB, PEO, SPE.

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## 1 Introduction

Lithium-ion battery (LIB) that can be recharged repeatedly is one of the most important technologies for storing energy. LIB is one of the most needed batteries because it can be recharged, is lightweight, durable, safe, and easily used in various forms [1]-[3]. In addition, its relatively high oxidation potential makes it ideal for high-energy-density batteries. However, suppose the lithium-ion battery uses an electrolyte solution. In that case, the contact between the lithium metal electrode and the electrolyte solution can cause problems such as leakage, fire, or explosion. Therefore, solid electrolyte polymers have been developed to replace liquid electrolytes.

Solid polymer electrolyte (SPE) is recognized as one of the viable solutions to ensure the safety of high-performance rechargeable lithium batteries. SPE has several advantages over liquid electrolytes, such as being non-volatile, non-flammable, easy to process, good chemical and electrochemical stability, and environmental friendliness. SPE has two functions: a medium for ion transport (an alternative to an electrolyte) and a separator between the cathode and anode to prevent short circuits. In addition, SPE plays an important role in the electrochemical system of

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the battery. The properties of SPE components, such as polymers and lithium salts, significantly impact battery performance. The lithium salt is involved in the conductive properties of the SPE, and the polymer is involved in the physical properties of the SPE, such as mechanical strength [4]-[7].

Polyethylene oxide (PEO) is one of the most studied polymers as a solid solvent for lithium salts because it has a flexible ethylene oxide segment and an oxygen ether atom, which has a strong donor character and can easily dissolve $Li^+$ cations. This polymer can also be an excellent SPE material for Polyvinylidene fluoride-co-hexafluoropropylene (PVDF HFP). PVDF HFP has almost the same properties as PVdF, but there are still differences between the two materials, one of which is the high fluoride content. The content of this element helps in the process of dissolving the lithium salt in the solvent [4].

In this study, we discussed the effect of adding PEO to manufacture SPE based on PVDF HFP-LiBOB on the structure, morphology, and conductivity. In addition, battery cell tests such as Electrochemical Impedance Spectroscopy (EIS) are carried out to determine the conductivity value of battery cells with a half-cell system, such as $LiFePO_4$ |SPE|Li.

## 2 Materials and Methods

The materials used in this research are polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), polyethylene oxide (PEO), $LiB(C_2O_4)_2$ (LiBOB), ethylene carbonate (EC), ethyl methyl carbonate (EMC), N,N-Dimethylacetamide (DMAC), ethanol, Lithium Iron Phosphate ($LiFePO_4$), Li-metal, dan $TiO_2$.

The first process begins with the manufacture of SPE, starting with making SPE without PEO. The process begins by mixing 0.75 g of PVDF-HFP and 0.05 g of $TiO_2$ into a glass beaker containing 15 ml of DMAC on a hot plate, then waiting until it is homogeneous. Then a slurry is formed. Then, the coating process of each sample will be carried out using the solution cast technique method by pouring the finished slurry onto the glass substrate while thinning it to a homogeneous thickness on the entire surface. The next process is drying the sample in an open room for five days until it is completely dry and forms a polymer sheet. Making SPE with PEO is the same as the process mentioned earlier; the difference is that only 0.25 g of PEO is added.

Furthermore, the process of making liquid LiBOB as an immersing solution was carried out in a glove box by dissolving 1.55 g of LiBOB with a ratio of EC: EMC equal to 1:1 on a hot plate, waiting for it to be homogeneous. The prepared dry polymer sheet was then dipped into a homogeneous electrolyte solution. After dipping, the sample was allowed to dry in a glove box.

Finally, the process of making lithium battery cells was conducted by preparing a positive case, cathode ($LiFePO_4$), PVDF HFP-$TiO_2$-LiBOB electrolyte polymer sheet (as well as separator), anode (Li-metal), spacer, spring, and negative case. The glove box engine is turned on, and the battery assembly process is carried out in the glove box (the pressure inside the glove box is controlled to 0.02 mbar). The coin cell battery is arranged in the glove box. The coin cell battery was pressed with a crimping machine MSK-110 with a pressure of 1000 Psi. Then the initial coin cell voltage was measured using a multimeter.

## 3 Results and Discussion

### 3.1 Manufacture of SPE

The thickness of the SPE (Solid Polymer Electrolyte) sheet was measured with a screw micrometer; the measurement results can be seen in Table 1.

**Table 1.** The Thickness of the SPE Sheet

| Sample | Material Name | Solvent | Thickness Before Dyed ($\mu$m) | Thickness After Dyed ($\mu$m) | Thickness Change (%) |
|---|---|---|---|---|---|
| SPE without PEO | PVDF - HFP/$TiO_2$ | EC: EMC | 363 | 251 | 11.2 |
| SPE with PEO | PVDF - HFP/PEO/$TiO_2$ | | 452 | 239 | 21.3 |

From the measurement results, it can be concluded that the smallest thickness before dyeing was found in the SPE sample without PEO of 363 m and the largest in the SPE sample with PEO of 452 m. In comparison, the smallest thickness after dyeing is found in the SPE sample with a PEO of 239 m and the largest in the SPE sample without a PEO of 251 m. The difference in thickness of each sheet can be caused by casting in dishes with different diameters. Changes in thickness produced before to after dyeing experienced thinning, such as 11.2% of SPE samples without PEO and 21.3% of SPE samples with PEO. From this change, it is clear that the SPE sample with PEO experienced a considerable change in thickness because in the SPE sample with PEO, there was PEO where when immersed in an immersing solution, PEO could dissolve in $Li^+$ cations [8] so that the SPE sample with PEO experienced considerable depletion.

The mass of the SPE sheet was measured with a digital balance; the measurement results can be seen in Table 2

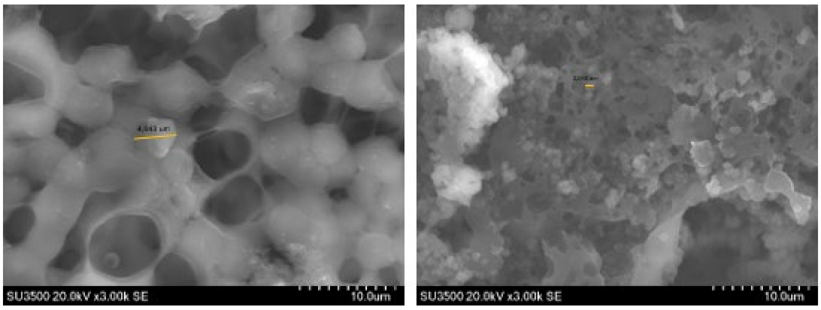
**Table 2.** The Thickness of the SPE Sheet

| Sample | Material Name | Solvent | Mass ($m_o$) before dyed (g) | Mass ($m_1$) after dyed (g) | Mass Change (%) |
|---|---|---|---|---|---|
| SPE without PEO | PVDF-HFP/$TiO_2$ | EC: EMC | 0.0542 | 0.0923 | 3.81 |
| SPE with PEO | PVDF-HFP/PEO/$TiO_2$ | | 0.1472 | 0,2600 | 11,28 |

From the measurements made, it can be concluded that the mass before and after dyeing experienced an increase in mass. The SPE sample without PEO experienced a mass change of 3.81% while the SPE sample with PEO experienced a mass change of 11.28%. The immersing process causes this change in mass, where when the sample is immersed in the immersing solution, it will affect the mass of the sample, namely the increase in the mass of the sample when it has been immersed. This increase is because when the immersing process happens, the composition in the solution blends with the sample and is also caused by the value of electrolyte uptake. Electrolyte uptake of SPE samples without PEO was 70.29%, and SPE with PEO was 76.63%. The higher the value of electrolyte absorption (electrolyte uptake), the more electrolyte solution will be absorbed [9]. Therefore, its mass increases after the sample are immersed in the immersing solution.

### 3.2 Manufacture of SPE (*Solid Polymer Electrolyte*)

Observations using a Scanning Electron Microscope (SEM) were carried out to see or determine the morphology on the SPE sheet. The reaction between $LiB(C_2O_4)_2$ with PVDF-HFP/$TiO_2$ and the addition of PEO can be observed by the differences in the surface morphology of each sample. Observations using an SEM for particles in each sample to determine whether there is agglomeration and pores so that the polymer materials bind to each other and form strong bonds. SPE surface morphology with solution cast technique. The results were obtained in a comparison of the surface of the SPE without PEO and with PEO at a magnification scale of 3000 times.



(a) (b)

**Figure 1.** Surface Morphology of (a) SPE without PEO (b) SPE with PEO

At the same magnification, it appears that the microstructure of the sheet shows a significant difference. Figure 1 shows the morphology of the SPE samples without PEO and with PEO having density changes. So, adding PEO is very influential in the structure of the SPE to be denser. All samples consist of small and large particles forming agglomerations with various particle shapes such as round, oval, and irregular. This agglomeration is caused by the solution not being homogeneous, so it is not evenly distributed. In the SPE sample without PEO, large particles gather to form one large material (bulk material). Likewise, in SPE samples with PEO, there are small particles. However, each sample still has porosity caused by trapped bubbles during the SPE sheet manufacturing process, and when it becomes a solid sheet, the bubbles burst and make the sheet have pores.

The material's morphology is a determinant to facilitate the movement of ions. In the structure of amorphous materials, ions can more easily move from one polymer chain to another in solid polymer electrolyte systems. The resulting polymer matrix must contain an amorphous phase for high ionic conductivity [10]. The results showed that the SPE sample with PEO has proven that the amorphous phase can increase its conductivity.

## 4 Conclusion

Solid polymer electrolyte (SPE) with and without Polyethylene oxide (PEO) was successfully synthesized using the solution cast technique. The addition of PEO affects the thickness and mass of resulted SPE. SEM analysis shows that the addition of PEO plays a role in forming the SPE membrane because the addition of PEO greatly affects the density of the SPE sheet. Furthermore, the results showed that the SPE sample with PEO has proven that the amorphous phase can increase its conductivity.

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