The effect of (TiO$_2$ and SiO$_2$) nano-filler on solid polymer electrolyte based LiBOB

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Abstract. Solid polymer electrolyte (SPE) is one of the most promising electrolytes to replace liquid electrolytes in the battery system to avoid leakage and to enhance the packaging efficiency. However, SPEs still have a much lower ionic conductivity compared to the liquid electrolyte. The purpose of this research is to investigate the effect of incorporating fillers on SPE to ionic conductivity characteristics and battery performance. The fillers employed in this study were SiO$_2$ and TiO$_2$ respectively 10 % in the ratio 4:1 of poly (vinylidene fluoride)-co-hexafluoropropylene (PVDF HFP) and lithium bis(oxalate)borate (LiBOB) compositions. The obtained SPE was characterized by using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), and Scanning Electron Microscope (SEM). This study revealed that 10 wt% SiO$_2$ concentrations provided ionic conductivity $2.42 \times 10^{-6}$ S cm$^{-1}$, higher than SPE with TiO$_2$ and without fillers. These results are confirmed by the CV results showing the highest reduction peak, current of -0.63 mA and voltage of 2.94 V, and discharge capacity of 47.8 mAh/g. In addition, SEM results reveal that the incorporated-SiO$_2$ SPE has porous morphology with diameter 2.8 um on average, assisting its intercalation process as well.

1. Introduction

The solid polymer electrolyte (SPE) is a kind of the electrolytes that enable to replace liquid electrolyte on a lithium-ion battery (LIB). The SPE consists of a combination of the polymer matrix and inorganic salts. The SPE has some advantages such as high compatibility to the other components, an anode, and cathode as well as its suitability to solve some problems caused by the liquid electrolyte in LIB systems such as packaging leakage and expansion volume [1]. The SPE takes place not only as an electrolyte but also as a separator which separates between the anode and the cathode in order to avoid occurring short circuit and forming lithium dendrite [2]. In addition, easy fabrication and flexibility are also key factors for researchers to evolve a new generation of LIBs, such as bendable lithium-ion batteries. However, the ionic conductivity and performance of SPE on LIB are inferior to those of liquid electrolyte.

Various combinations of the polymer matrix and lithium salt have been conducted to improve the SPE performance in LIB. Recently the SPE based lithium bis(oxalate) borate (LiBOB) attracts researchers to extend its properties. This salt is selected due to its excellent characteristics for LIB,
such its ability to form a stable solid electrolyte interface (SEI), high compatibility to the current collector (Al metal), and easy synthesis [3–5]. In addition, LIBs employed LiBOB as lithium salts have a more stable storage capacity compared to that of LiPF₆ [6]. LiBOB-based SPE was successfully prepared by poly (vinyl alcohol) (PPA) matrix resulting in ionic conductivity around $10^{-4}$ S cm⁻¹ [7]. Poly(vinylidenefluoride)-co-hexafluoropropylene (PVDF-HFP) dissolved in carbonate solvents succeed to prepare on LiBOB-based SPE as polymer matrix because of its high fluoride content which can assist salt lithium solubility [8].

Ceramic oxide, ZrO₂, and the plasticizer, polyethylene oxide (PEO), were incorporated to SPEs based LiBOB in order to increase their ionic conductivity and performance [9, 10]. The other ceramic oxide such as titanium oxide (TiO₂) was combined as fillers for LiClO₄-based SPE with polymer matrix polyethylene oxide-polymethyl methacrylate (PEO-PMMA) as well [11]. The addition of this filler could decrease the crystallinity of SPE in which charge could be transferred easily. The silicon oxide (SiO₂) was filled on compositing PVDF-based HFP resulting porous composite with diameter 1.14 μm on average. The formation of this pore may facilitate the process of intercalation lithium ions on LIB [12].

In this article, it is discussed to investigate the effect of fillers on SPE properties. The combinations of PVDF-HFP/PVDF, LiBOB, and TiO₂/SiO₂ with ratio 72:18:10 in wt%, were prepared and cast by the doctor blade. The ingredients were dissolved in $n,n$-dimethyl acetamide (DMAC) and continuously stirred at 60°C for three hours. The SPEs were then sandwiched into a coin cell-based half cell.

2. Experimental Methods

2.1. Materials

Lithium bis(oxalato) borate (LiBOB) as lithium salt of SPE was purchased from Sigma Aldrich. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF HFP, Sigma Aldrich) pellets and Poly(vinylidene fluoride) (PVDF) with purity >98% and a molecular weight >180,000 (GPC) were employed as polymer matrixes. N,N-dimethylacetamide (DMAC purity >99%, Merck) was considered as solvent. 0.5 M LiBOB dissolved in EC: EMC (3:7) purchased from Merck with purity >98% was also considered as the activator. TiO₂ (Sigma Aldrich, nanopowder size 21 nm, >99.5%) and SiO₂ were as nanofillers.

2.2. Sample solid polymer electrolyte and half coin cells preparation

The materials except solvents were evaporated their water contents at 70°C for 24 hours. Initially, the PVDF HFP/PVDF was dissolved in 8 mL DMAC on a hotplate at 60°C while stirred at 250 rpm for 45 minutes. The mixture was added LiBOB and kept stirring then followed by the fillers, TiO₂ and SiO₂. After the slurries were blended homogeneously, they were cast on the glass and dried at room temperature. The composition of the mixture was shown in table 1.

The dried SPEs were sandwiched by an electrode, lithium iron phosphate (LiFePO₄) as a cathode and lithium metal as the anode. The assembling was conducted in a glove box filled with argon gas at room temperature. Before crimped into a coin cell, the SPEs were dropped by an activator in order to activate the lithium salt.

2.3. Characterization

The dried SPEs were characterized by an SEM to investigate their surface morphology. The coin cells employed by the SPE were measured by their ionic conductivity properties by EIS (HIOKI 5322-50 LCR HiTESTER) along frequency 0.6 - 20 kHz. The electrochemical performance of coin cells was also evaluated by cyclic voltammetry (CV) within the scan rate of 0.05 mV/s over the voltage range, 0.05 – 4 V for three cycles.
Table 1. Composition of SPEs

| Sample | Host polymer and the lithium salt | Filler |
|--------|----------------------------------|--------|
| A      | PVDF HFP + LiBOB                | -      |
| B      | PVDF HFP + LiBOB                | TiO₂   |
| C      | PVDF HFP + LiBOB                | SiO₂   |
| D      | PVDF + LiBOB                    | SiO₂   |

3. Results and discussion

LiBOB-based SPEs were successfully prepared by solution casting, except for sample C, the composition of which was PVFF HFP + LiBOB + SiO₂. The composition created such a perforated SPE that it was conveniently not measured and tested by EIS and CV because it could cause a short circuit in the cell. The perforation may be affected by the H₂O content from the reaction between silicon dioxide and fluoride acid, by which a reaction between fluoride contained in PVDF HFP and DMAc produces. The H₂O evaporates during the drying process and forms some perforation in the SPE [13].

3.1. EIS measurement

The first test conducted to coin cell employed SPE based LiBOB was EIS, the measurement to investigate the properties, for instance, ionic conductivity and diffusion coefficient. The ionic conductivity can be calculated by a simple equation, \( \tau = l / (A*R) \), where \( \tau \), \( l \), \( A \), and \( R \) respectively represent ionic conductivity, SPE thickness, SPE-electrode contact area, and SPE resistance. The ion diffusion coefficient is allowed to be calculated as executed by Wang, et al. from real impedance data at low-frequency region using the following equation [14].

\[
D = 0.5 \sqrt{\frac{RT}{AF^2 \sigma_n C}}
\]

where \( D \) means the diffusion coefficient, \( R \) and \( T \) represent gas constants and absolute temperature. \( A, F, C \), and \( \sigma_n \) exhibits the electrode area, Faraday coefficient, \( Li^+ \) molar concentrations, and Warburg coefficients. The summery of ionic conductivity and the ion diffusion coefficient calculation are listed in table 2. From table 2, it is clear that the cell used SPE based LiBOB incorporated by 10wt% SiO₂ and TiO₂ provides insignificant changes, especially ionic conductivity value, still in the order of \( 10^{-6} \) S.cm⁻¹. These properties seem better than that of SPE incorporated by ZrO₂ filler, conducted by Wigayati, et al. [10].

The ionic conductivity of the cell increases when it utilizes SPE added by 10wt% SiO₂. However, the ionic conductivity decreases since the cell employed the SPE occupied 10wt% TiO₂ as the filler. These properties affect the charge transfer of Li from the anode to the cathode, as seen from the trends of \( Li^+ \) diffusion coefficient which proportionally look like to those of the ionic conductivity properties.

Table 2. The ionic conductivity of SPEs based LiBOB

| Sample | Ionic conductivity (S.cm⁻¹) | Warburg Coefficient (Ω cm² ⁰.⁵) | \( D_{Li} \) (cm² s⁻¹) |
|--------|-----------------------------|----------------------------------|-------------------------|
| A      | \( 2.02 \times 10^{-6} \)   | 311.34                           | \( 9.2 \times 10^{-20} \) |
| B      | \( 1.27 \times 10^{-6} \)   | 786.97                           | \( 1.4 \times 10^{-20} \) |
| D      | \( 2.42 \times 10^{-6} \)   | 154.89                           | \( 3.7 \times 10^{-19} \) |
3.2. Electrochemical test

The cyclic voltammetry test was considered to conduct in this study in order to analyse the electrochemical performance using LiFePO₄/Li⁺ cell employed SPE based LiBOB as electrolyte and separator. The cells were examined after the cell had completely been measured by EIS. Figure 1 displays the cell performance profile which had been recorded for a cycle with scan rate of 50 mV/s. From the voltammogram, it can be seen that the cells with the prepared SPE still reveals a single peak, exactly reduction peak. This single peak indicates that the electrochemical performance occurring within the cell appears irreversible [15]. These circumstances indicate the unbalance reactions within the cell, oxidation, and oxidation reactions [10].

When the voltammogram is enlarged in the particular part, especially at the reduction peak as shown in figure 1 (b), it obviously demonstrates that the addition of fillers such as TiO₂ and SiO₂ exhibits significant changes. The changes might be provoked by the truly activated cation, Li⁺. The reduction peak takes place at a different voltage, 2.71 volts for SPE without filler, 2.93 volts, and 2.94 volts for SPE with TiO₂ and SiO₂ filler, respectively. The voltages imply the electrode voltage during the reduction reaction in the battery cell. When we observe the sharpness of the reduction peak, the cell electrolyzed by SPE-10wt% SiO₂ is considered as the highest peak, followed by that of TiO₂ filler and without filler. This current peak affects the discharge capacity of a battery cell [16]. The sharper peak marks an increasing discharge capacity, as presented in figure 1 (c). Discharge capacities for cells applied SPE without filler, with TiO₂, and SiO₂ are 2.35, 40.6, and 47.8 mAh g⁻¹, respectively.

![Image](image-url)

**Figure 1.** (a) Electrochemical profile of SPE based LiBOB, (b) its magnitude and (c) graph of discharge capacity.
3.3. Morphology of SPE

In addition to EIS and CV characterization, the SPE morphology was carried out to observe the effect of filler on SPE morphology. On the other hand, LiBOB as lithium salt solubility can be analyzed on the surface of the morphology. Figure 2 shows the morphology of SPE both without filler and with fillers (TiO$_2$ and SiO$_2$). From the image of the morphology clearly appears a significant change. SPE without filler is slightly found a few pores accompanied by particles with size 9.5 µm in diameter. These particles are regarded as LiBOB particles which do not dissolve completely especially in the polymer solvent. The insoluble lithium salt can reduce the amount of Li$^+$ as cations in the SPE, which affect the process of transfer of Li$^+$ ions. Morphology changed after the added filler TiO$_2$ and SiO$_2$.

The particle size decreased in SPE morphology after 10wt% TiO$_2$ filler was added with a particle diameter size of 1.6 µm on average. It is probably due to intermolecular interactions between LiBOB and TiO$_2$. Nevertheless, the morphology owns an increased amount of pore distributions after SiO$_2$ incorporated into the SPE with pore diameter size 2.8 µm on average. Perhaps the pores established due to the reaction between SiO$_2$ and fluoride which PVDF has so succinctly that it could not create any perforation on SPE morphology. The porous structure will take up the activator, LiBOB solution in EC:EMC (3:7 v/v), of the lithium salt, resulting in much-activated lithium and ease of Li$^+$ intercalation process.

4. Conclusions

The SPE based LiBOB with fluorinated polymers (PVDF/PVDF HFP) with TiO$_2$ and SiO$_2$ as fillers were successfully prepared. However, the SPE which consist of PVDF HFP and LiBOB with 10% SiO$_2$ produces a perforated sheet. The ionic conductivity of cell employed SPE based LiBOB without filler as well as with the TiO$_2$ and SiO$_2$ fillers reveals 2.02 × 10$^{-6}$, 1.27 × 10$^{-6}$ and 2.42 × 10$^{-6}$ S/cm, respectively. In addition, the CV results demonstrate that all electrochemical performance of cell utilized the SPE are still irreversible. The discharge capacity of the cell with SPE without filler as well as with TiO$_2$ and SiO$_2$ are represented by 2.35, 40.6 and 47.8 mAh/g, respectively. In the other hand,
incorporation TiO$_2$ as the filler of SPE based LiBOB can also reduce the particle size in the morphology, approximately 1.6 μm, while the addition of SiO$_2$ filler generates a porous SPE with a diameter 2.8 μm in average.

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