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Polyethylene glycol incorporation on doctor blade and screen printing cast solid polymer electrolyte based PVDF HFP–LiBOB

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Abstract. Solid polymer electrolyte (SPE) is considered as one of the most attractive and promising electrolytes that enable to solve a leaking-packaging problem. Nevertheless, this electrolyte still exhibits poor performance and ionic conductivity. The objective of this study is to investigate the effect of PEG incorporation on the ionic conductivity properties and its performance in the battery. The Solid polymer electrolytes (SPEs) were fabricated from poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF HFP), lithium bis(oxalate) borate (LiBOB) and polyethylene glycol (PEG) with a ratio of 72%, 18%, 10%. The slurry was cast by the doctor blade (DB) and screen printing (SP) and dried at 27°C. The SPEs obtained were characterized by Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), and Scanning Electron Microscope (SEM). The ionic conductivity increased with the addition of 10% PEG for the sample prepared by the DB method, while it decreased in the sample prepared by SP method. The CV result reveals that the SPE cast by SP creates double reduction peaks and all cells still have an irreversible system. The other hand, 10% PEG incorporation, SPEs morphologically appear to decrease particle size on the surface of SPE.

1. Introduction

All Solid State Battery is a battery system developed recently in order to meet energy storage in demand such as a smartphone, laptop, camera, electrical vehicle, etc. One of its main components is a solid polymer electrolyte (SPE) which takes a place not only as an ionic conductor but also as separator dissociating electrode in order to avoid occurring short current [1]. SPE becomes one of the most promising electrolytes that enable to solve a leaking-packaging problem caused by the liquid electrolyte. There are various advantages belonging to SPE, for instance having excellent versatility, high compatibility with an electrode, lightweight, and simple fabrication. However, SPE is still much more inferior conduction in ionic than that of a commercial electrolyte approximately $\sim 10^{-2}$ S/cm (LiPF₆) [2].

SPE is generally defined as the dissolution of lithium salt and polymer in a solvent [3]. Lithium bis(oxalate) borate (LiBOB) is one of the new lithium salts applied to the lithium-ion battery (LIB). This lithium salt has higher capacitance stability than that of commercial electrolyte (LiPF₆) [4]. LiBOB has such a high thermal stability, up to 302°C, that it is appropriately applied to LIB for an electrical vehicle. Besides lithium salt, Amount of polymers have already been used as matrix polymer to prepare SPE based LiBOB, for instance, methyl-cellulose (MC) [5], and poly(vinyl alcohol) (PPA) [6]. Fluorinated polymers such as poly(vinylidene fluoride) (PVDF) or poly(vinylidene fluoride)-co-



hexafluoropropylene (PVDF HFP) are considered as the excellent polymer matrix for SPE. These polymers have a high dielectric constant of approximately 8.5 and contain fluorine. These properties could assist the lithium salt solubility [7, 8]. Chowdhury, et.al prepared SPE based PVDF-LiBOB in N-methyl-2-Pyrrolidone (NMP) [9].

Additives, ceramic oxides, and plasticizer, were also incorporated by some researchers to SPE in the recent decade. SPE based PVDF-LiBOB assisted by Titanium Oxide (TiO₂) [10], and ZrO₂ [11] were carried out. These fillers can interact with intermolecular polymer chain decreasing the crystallinity of the SPE and improve the mechanical properties of the SPE. Polyethylene glycol (PEG) is considered as a polymer matrix on SPE based LiClO₄. The polymer owns a short polymer chain which enables a fast segmental motion enhancing the ionic conductivity [12]. Guzmán-González *et al.* [13] reported an investigation about ion transport in SPE employing boron sp³ and various-chain PEG as bridges. They found that the electrochemical stability was slightly decreased as the chain length of PEG increased [13]. In this paper, incorporation of PEG on SPE based PVDF HFP-LiBOB is discussed. SPE is cast by two methods, solution casting by the doctor blade and screen printing, in order to compare the thick (>100 μm) and thin (<100 μm) SPE. The SPE was sandwiched with electrodes than sealed into a half cell. Electrochemical analyses such as Electrochemical Impedance Spectroscopy (EIS) as well as Cyclic Voltammetry (CV) are decided to investigate its impedance and electrochemical performance in a battery system.

2. Methods

2.1. Materials

Amount of specific material were used in this study such as lithium salt, Lithium bis(oxalato) borate with a high purity (LiBOB, Sigma Aldrich). Poly(vinylidene) fluoride-co-hexafluoropropylene (PVDF HFP, Sigma Aldrich) were considered as the polymer matrix of SPE. N-dimethylacetamide (DMAC, purity >99%, Merck) was employed as the polymer solvent. Polyethylene glycol (PEG) (Merck, weight 6000) was used as the additive. The activator of lithium salt was 0.5 M LiBOB in ethyl carbonate (EC) and ethyl methyl carbonate (EMC) with the ratio 1:1 (w/w) with well purity purchased from Merck.

2.2. Solid polymer electrolyte and a half cell preparation

All starting materials employed in this experiment should be heated in an oven at 70°C for overnight in order to evaporate some H₂O content in each precursor. The percentage of the polymer matrix, lithium salt, and plasticizer is respectively presented by 72%, 18%, and 10% in weight. The PVDF HFP and LiBOB were respectively stirred in 2 mL DMAC on a hotplate (KAC- MAG HS-7) at 60°C and at 250 rpm. The mixture was added PEG and kept stirring. After the homogeneously dissolved materials, the slurries were cast on the glass by the doctor blade and a handmade screen printing then dried at room temperature and cut into a disk with 20 mm in diameter. The other sheets of SPE were also shaped for morphology characterization.

A half-cell was arranged by various parts such as the cathode, commercial lithium iron phosphate (LiFePO₄) (LFP), the dried SPE, and an anode, lithium metal on Argon atmosphere in a glove box. The SPEs were dropped by an activator for the lithium salt activation then were crimped into the coin cell.

2.3. Sample characterization

The ionic conductivity measurement of the half coin cells was carried out using HIOKI 5322-50 LCR HiTESTER under room temperature with a range frequency 0.1 Hz-20 kHz. Cyclic voltammetry (WBCS3000) investigation was conducted to evaluate the electrochemical system occurred in the coin cell scanned by potential rate 0.05 V/s over the voltage range, 0–4.0 V. The surface morphology was also analyzed by Scanning Electron Microscope. One of the SPEs blended by 10% PEG was captured after CV measurement in order to further observation.

3. Result and Discussions

3.1. Electrochemical Impedance Analysis

The EIS-characterization result of the coin cells is displayed in figure 1. It provides information regarding impedance value which was subtitled to a simple equation, $\sigma=l/(R_b \cdot A)$, to obtain ionic conductivity (σ), where l , A , and R_b respectively represent thickness of the SPE (cm), electrode-electrolyte contact area (cm^2), and bulk resistance of the cell (ohm). The impedance of every cell was acquired by picking the intersection point of a semicircle to the real-impedance axis (Z') or x-axis. Table 1 exhibits the ionic conductivity property of the SPE-based cell.

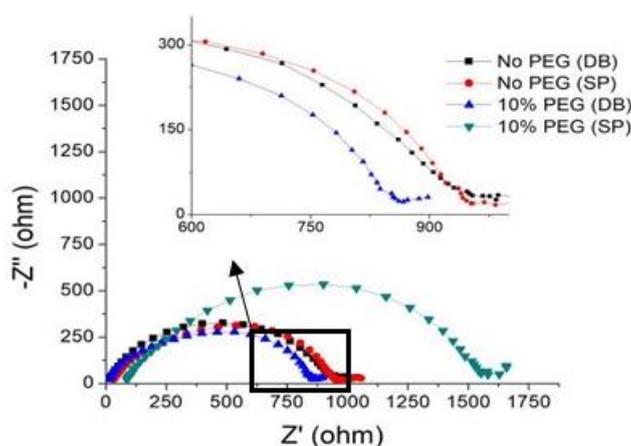


Figure 1. Nyquist plot for coin cells employed the SPE cast by DB and SP.

It appears some decrease of the resistant of PVDF HFP-LiBOB based SPE cast by DB when incorporated by 10% PEG, from 9.84×10^{-2} ohm to 8.67×10^{-2} ohm. Nevertheless, the SPE cast by SP seems some incensement of its resistant, from 9.83×10^{-2} ohm to 1.58×10^{-3} ohm. As it is known that ionic conductivity is inversely proportional to resistant. Table 1 reveals the ionic conductivity value for every cell. It is clear that the thick SPE, which was cast by SP, has better ionic conductivity than that of the thin one.

Table 1. The conductivity value of PVDF HFP–LiBOB based SPEs prepared by DB and SP.

Sample	Thickness (μm)	Conductivity (S/cm)
(A) 0% PEG (DB)	40	2.02×10^{-6}
(B) 10% PEG (DB)	70	4.02×10^{-6}
(C) 0% PEG (SP)	190	9.61×10^{-6}
(D) 10% PEG (SP)	180	5.66×10^{-6}

10% PEG incorporation to PVDF HFP-LiBOB based SPE cast by both DB and SP still contributes an inferior ionic conductivity (10^{-5} - 10^{-6} Scm^{-1}). However, this result has higher ionic conductivity than that of PVDF-LiBOB based SPE incorporated by PEG and ZrO_2 [14, 15]. These results can be affected by PVDF HFP which owns fluoride more than that of PVDF. It could assist the drawback of LiBOB such as poor solubility in polymer solvent (DMAC).

3.2. Electrochemical analysis

Generally, researchers have widely utilized CV to investigate the performance of a cell. This characterization may give some information regarding electrochemical system occurred in the cells which were tested, for instance, reversibility of the cells. The reversibility can be ensured by couple peaks, reduction and oxidation peaks, formed in the voltammogram [16]. Figure 2 represents CV-characterization result of the cells applied PVDF HFP–LiBOB based SPE by $\text{LiFePO}_4|\text{Li}$. The test was carried out after the cells tested by EIS.

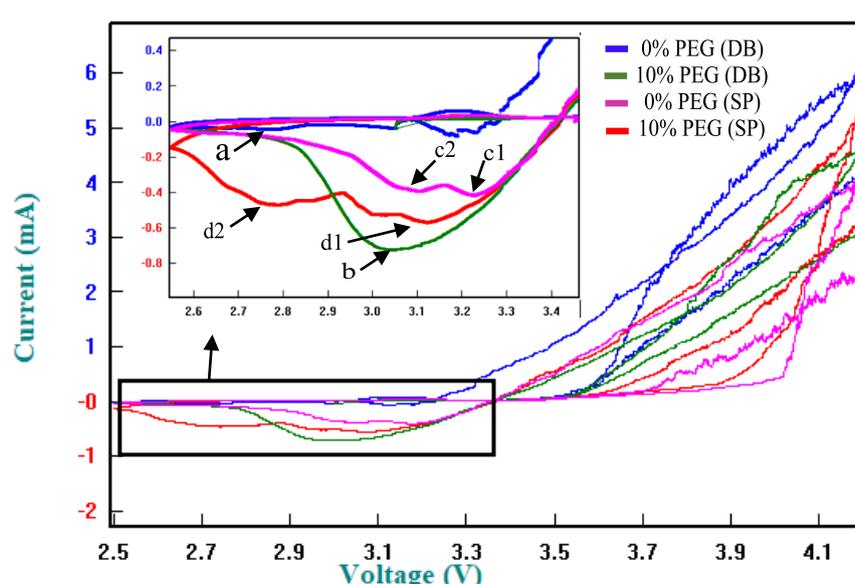


Figure 2. Cyclic voltammogram of coin cell employed SPE based LiBOB.

From voltammogram, it can be seen that all tested cells exhibit an irreversible system, which is determined by the existence of a single peak, exactly reduction peak. Mixing 10% PEG to SPE, cast by either DB or SP, significantly increases the sharpness of reduction peak. The sharp peak indicates a fast redox reaction happened in the cells than that of the dull peak [17]. Each cell does not have a shape peak in common, where every cell utilizing SPE cast by SP creates double reduction peaks, namely c1 (3.17 volt) and c2 (3.05 volt) for 0% PEG sample, and d1 (3.07 volt) and d2 (2.74 volts) for 10% PEG sample. While each cell sandwiched by SPE cast by DB, they reveal a single reduction peak, namely a (2.73 volt) and b (2.99 volts).

3.3. Scanning electron microscope (SEM)

In this work, the SPEs were also observed by SEM in order to investigate the morphology of SPE mixed by PEG. Figure 3 displays the morphology of DB-or-SP cast SPE based PVDF HFP–LiBOB blended by both 0% PEG and 10% PEG. In addition, LiBOB solubility can also be ensured by investigating size particles appeared on the surface of SPE through this characterization. Figure 3a shows the surface morphology of SPE without mixing PEG, where some particles which have diameters around 9.5 μm appear. However, when 10% PEG was blended to the SPE as presented in figure 3b and 3c, the particles have decreased in size for SPE cast by both SP and DB, namely 1.6 μm and 1.3 μm . The particles are supposed to be LiBOB, which consummately does not dissolve in DMAC, especially in polymer-solvent [15]. It is thought because the polymer matrix and plasticizer contained in the SPE has good solubility in the solvent (DMAC) [18]. Lithium salt which possesses poor solubility can indicate low intercalation due to poor Li^+ presence. The morphology of 10% PEG

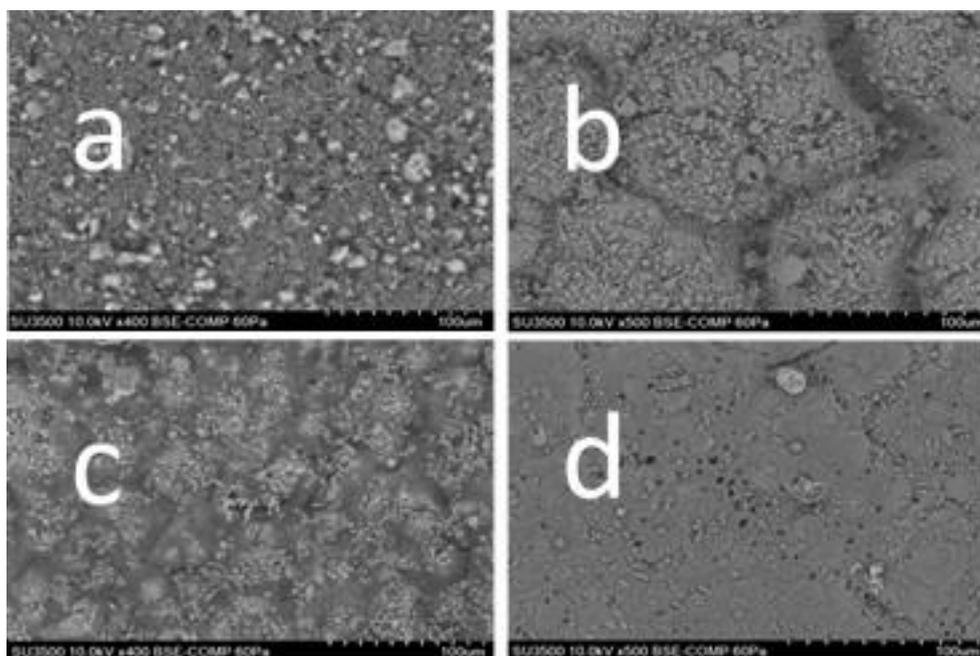


Figure 3. Surface morphology of PVDF HFP-LiBOB based SPE (a) without PEG via DB, (b) with PEG via SP, (c) with PEG via DB before CV test, and (d) with PEG via DB after CV test.

incorporated SPE cast by DB also was investigated after the samples were tested EIS and CV. Some changes occurred, where the surface morphology becomes porous (2.5 μm in average diameter) due to an activation process. On the other hand, some damages do not exist in the morphology of the SPE, because plasticizer such as PEG may increase the mechanical strength of the SPE [12].

4. Conclusions

Preparation of PVDF HFP-LiBOB based SPE blended PEG and cast by both DB and SP was successfully carried out. In this study, ionic conductivity is affected by not only the addition of 10% PEG but the thickness of SPE as well. The CV result reveals that the SPE cast by SP creates double reduction peaks and all cells still have an irreversible system. The other hand, 10% PEG incorporation, SPEs morphologically appear to decrease particle size on the surface of SPE as well.

Acknowledgments

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