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The Effect of LiBOB Addition on Solid Polymer Electrolyte (SPE) Production based PVDF-HFP/TiO₂/LiTFSI on Ionic Conductivity for Lithium-Ion Battery Applications



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Abstract

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Article Info

Received: 30th August 2021 Revised: 24th January 2022 Accepted: 25th January 2022 Online: 31st January 2022 Keywords: SPE; solution casting; LiBOB, LiTFSI; conductivity SPE (Solid Polymer Electrolyte) is an alternative to substitute conventional liquid electrolytes as it has a better safety level and has been produced using the solution casting method. An effort to increase the SPE conductivity of the PVDF-HFP/TiO $_2$ / LiTFSI system has been carried out by adding LiBOB as an additive. LiBOB (lithium bis(oxalate) borate) is a salt compound that can interfere with the crystallization process of polymer chains, so it is expected to increase ion conductivity. However, the results showed a decrease in the conductivity from 3.643 x 10⁻⁵ S/cm to 8.658 x 10⁻⁶ S/cm. These results were proven by the XRD, FTIR, SEM, and TGA characterization. Based on XRD (X-ray Diffraction) analysis, the addition of LiBOB increased the crystallinity phase. The results of the SEM (Scanning Electron Microscope) analysis showed that the pore size was partially reduced, the distance between the pores became longer, and the pore closure occurred due to agglomeration. The FTIR (Fourier Transform Infrared spectroscopy) analysis showed the interaction of LiBOB salts in the PVDF-HFP/LiTFSI/TiO2 system, and based on TGA (Thermogravimetric Analysis) analysis, the addition of LiBOB affected the heat stability of the SPE. The CV (Cyclic Voltammetry) analysis showed that the addition of LiBOB in the SPE system could reduce the reversibility and magnitude of the current.

1. Introduction

Nowadays, the need for energy storage systems such as batteries supercapacitors continues to increase along with electric transportation and electronic equipment development. SPE (Solid Polymer Electrolyte) as an alternative to conventional liquid electrolyte has received much attention for researchers to develop because it has a better safety level and a flexible shape, can prevent the growth of lithium dendrites, and is easy to manufacture [1].

SPE is formed from a polymer matrix with alkali metal ions as its charge source. Ions with low atomic mass, such as lithium-ion (Li⁺), will more easily undergo the process of charge transfer. This charge transfer occurs due to segmental relaxation, where the charge is transferred from one segment to another in the polymer matrix. Charge transfer is more effective when the polymer matrix is amorphous [2]. In the amorphous phase of polymer matrix, there is more free spaces which allow more ions movement when compared to the crystalline phase of polymer matrix. The weakness of SPE is that the ionic conductivity is lower than the liquid electrolyte, which is around 10⁻⁸ to 10⁻⁵ S.cm⁻¹ at room temperature. The requirements for ion conductivity in SPE for battery applications are 10⁻⁴ Scm⁻¹[3].

SPE is a solid matrix electrolyte, a solid solution of alkali metals in a polymer [4]. Lithium batteries using SPE membranes have more excellent safety, a structure that can be made thinner and more flexible. Wright *et al.*, (1975), had developed an SPE made from a mixture of polyethylene oxide (PEO) and salts of alkali metals [5]. PEO was developed into SPE because it had high ionic conductivity, low toxicity, and relatively high chemical stability. However, PEO polymer is brittle and relatively

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expensive. Therefore, SPE membranes have been developed with high conductivity, strong mechanical properties, thermal stability and can be produced reasonably. One approach to increase the amorphous phase at room temperature is to disperse nanoparticles or ceramic particles into a polymer matrix [6]. The metal oxides that can be used include SiO₂, Al₂O₃, ZnO, CeO, TiO₂, Fe₃O₄, and ZrO₂ [7].

The current focus is on improving ionic conductivity, thermal and chemical stability, and mechanical strength. Various methods that have been done to enhance and change SPE properties are the incorporation of polymers, electrolyte salts, and the addition of additives, which are strategies to reduce/repress crystallinity or increase amorphous properties conductivity increases [8]. Tripati et al., (2012) combining PVdF-HFP and PMMA, adding NaI, with the solution casting method, the conductivity value was 1.67 x 10⁻² (S/cm) [9]. The combination of LiTFSI and LiNO₃ by electrospinning method, PVdF-HFP polymer, and SiO₂ as ceramic filler showed a conductivity of 1.3 x 10⁻³ S/cm [10]. Lestariningsih et al., (2017) have reported the manufacture of SPE by solid casting method using PVdF-HFP as polymer, LiBOB as electrolyte salt, and TiO₂ as ceramic filler. The conductivity obtained with a composition of 2% by weight of TiO₂ can be increased even though it is still below the required value for SPE membranes [11]. The addition of SN (succinonitrile) to the PVdF HFP/LiBOB polymer system with the solid casting method obtained a 6.711x10⁻⁸ S/cm [12]. The next effort to increase the conductivity is to modify the type of electrolyte salt added. This salt modification study is based on previous research conducted by Chen et al., (2014) [13]. The results showed that the liquid electrolyte with LiTFSI and LiBOB components in the Li/LiFePO4 half-cell could reach 1000 cycles, while the electrolyte with LiPF₆ components could not reach 1000 cycles at a high temperature of 60°C. The salt mixture also can reduce corrosion on battery electrodes [13]. LiBOB is a large anion that can directly interfere with the crystallization process of the PEO chain, thereby promoting an increase in the amorphous region with a consequent increase in the Li⁺ conductivity [14, 15]. However, three lithium salts with larger anions have been developed, such as LiN(CF₃SO₂)₂ (LiTFSI), LiN(C₂F₅SO₂)₂ (LiBETI), and LiC (CF₃SO₂)₃ (LiTFSM), which also offer higher Li⁺ conductivity than LiBOB. However, these salts are not preferred for lithium-ion batteries because they tend to corrode aluminum current collectors [15]. Meanwhile, Lithium bis (trifuoromethanesulfonyl) imide [LiTFSI, LiN(CF₃SO₂)₂] salt is an alternative salt to replace LiPF₆ (lithium hexafluoride phosphate) salt, which is commonly used today. However, the use of LiTFSI salt can cause corrosion of the positive electrode aluminum current collector (Al foil) when used at a voltage of about 3.7V vs Li/Li+ [16, 17]. Poly(vinylidene fluoride-cohexafluoro-propylene (PVdF-HFP) as a polymer matrix has excellent chemical stability due to the vinylidene crystalline phase (Vdf) and plasticity, mainly supported by the amorphous hexafluoropropylene (HFP). The strong electron attractant (-CF) in PVDF-HFP makes this polymer very anodic stable [8].

This paper will study the effect of adding LiBOB electrolyte salt in SPE system PVdF-HFP/TiO₂/LiTFSI on ionic conductivity and electrochemical properties. The method used in the manufacture of SPE is solid casting. Characterizations carried out include EIS, XRD, FTIR, SEM, TGA, and cyclic voltammetry (CV).

2. Methodology

2.1. Tools and Materials

The tools used in this study include glassware, scales, hot plates (heaters), and instruments, such as XRD (X-ray Diffraction), FTIR (Fourier Transform Infrared spectroscopy), SEM (Scanning Electron Microscope), TGA (Thermogravimetric Analysis), LCR meter HIOKI 3532150, and WBCS3000 automatic battery cycler. The materials were PVdF-HFP (poly (vinylidene fluoride-hexafluoropropylene) as polymer, LiTFSI (Lithium bis-trifluoromethanesulfonimide) and LiBOB (lithium bis(oxalate) borate) as salts, these products were from Sigma Aldrich. Titanium oxide (TiO₂) is used as a filler and DMAC (N,N-dimethylacetamide) as a solvent; both products were from Merck. LTO (Lithium Titanium Oxide) cathode sheet, Lithium metal, and coin cell were MTI products.

2.2. Solid Polymer Electrolyte (SPE) Production

SPE production was conducted using the solution casting method. The manufacture of a viscous solution (slurry) was begun by dissolving the electrolyte salt LiBOB-LiTFSI and TiO₂ into the DMAC solvent until it dissolved with various compositions, as shown in Table 1. The mixing process was carried out on a hotplate at \pm 80°C with a rotation of 240 rpm. The next step was to add PVdF-HFP as a polymer matrix with the same process. Mixing all the ingredients to form a viscous solution (slurry) was carried out for 6 hours. The resulting viscous solution was cast on a glass board/substrate and allowed to dry at room temperature for 3–4 days, then stored in a dry box before characterization.

2.3. Solid Polymer Electrolyte (SPE) Characterization

The characterization of the SPE samples in this study included measuring the ionic conductivity using EIS (Electrochemical Impedance Spectroscopy) with the LCR meter HIOKI 3532150 chemical impedance meter. The test sample was made in the form of a sandwich in which the polymer sample was placed between 2 stainless steel plates as electrodes by the EIS method. The shape of the phase determined using XRD brand Rigaku Smart Lab type, with a target Cu K λ (λ =1.5406Å) with an angle range of $2\theta = 0-60^{\circ}$. FTIR spectroscopy Thermo scientific Nicolet iS-10 type was used to determine the chemical interaction between salt and polymer by observing the shift in the absorption band, and the observations were carried out at a wavelength of 4000-500 cm⁻¹ with the ATR method. The morphology of the SPE samples was observed using a Jeol JED Scanning Electron Microscope (SEM). Thermal stability was observed using Linseis TGA with a heating rate of 10°C min⁻¹ in the temperature range of 0-400°C. Electrochemical properties were observed by CV using the WBCS3000 automatic battery cycler. The test sample was made in a Li₄Ti₅O₁₂/Li⁺ half cell.

2.4. Measurement of Ionic Conductivity

The ionic conductivity test is obtained from impedance measurements using EIS at 100,000 Hz–0.1 Hz. The impedance measurement data are the real part (R') and the imaginary part (R'') that create the Nyquist plot. The resistance of SPE (Rb) can be obtained from the Nyquist plot. SPE plots based on PVdF-HFP/TiO₂/LiTFSI from various variations of LiBOB addition will form a semicircle. The electrolytic resistance (Re) is the starting point on the semicircle. The distance between Re to the endpoint represents the charge transfer resistance (Rct). The width between Re and Rct determines the ionic conductivity of the battery. The ionic conductivity of SPE can be determined using the following formula:

$$\sigma = t / (Rb \times A) \tag{1}$$

Where t is the thickness of the SPE sheet (cm), Rb is the solid electrolyte polymer resistance (Ohm), and A is the surface area of the sample (cm^2) [18].

3. Results and Discussion

This study consisted of 3 samples with varying amounts of LiBOB added to the SPE with the composition shown in Table 1.

Table 1. SPE sample composition

Sample	Electrolyte material composition (% weight)					
	PVdF-HFP	TiO ₂	LiTFSI	LiBOB		
A-0% LiBOB	70	2	28	0		
B-5% LiBOB	70	2	23	5		
C-14% LiBOB	70	2	14	14		

3.1. Electrochemical Impedance Spectroscopy (EIS) Analysis

The Nyquist curve of SPE samples containing PVDF-HFP/TiO₂/LiTFSI with variations in the addition of LiBOB: A) A-0% LiBOB, B). B-5% LiBOB and C). C-14% LiBOB forms a semicircle curve, as shown in Figure 1. The analysis results using the ZView software obtained the value of Rb (electrolyte resistance/resistance) as in Table 2. The conductivity value can be calculated using the following formula: $\sigma = t / (Rb \times A)$.

In this paper, A-0% LiBOB had the smallest value of electrolyte impedance. The increase in impedance due to the addition of LiBOB salt will increase the crystallinity phase (from XRD analysis), which results in the movement of Lithium ions being hampered; hence a significant resistance is required. Bode plot analysis was used to support the analysis of data from the Nyquist magnitude curve related to the of the impedance/resistance of the electrolyte (Re) at the highest frequency to determine the value of ionic conductivity. Figure 1 shows that A-0% LiBOB at the lowest frequency had the highest impedance resistance. In contrast, the B-5% LiBOB and C-14% LiBOB at the same low-frequency impedance resistance decreased.

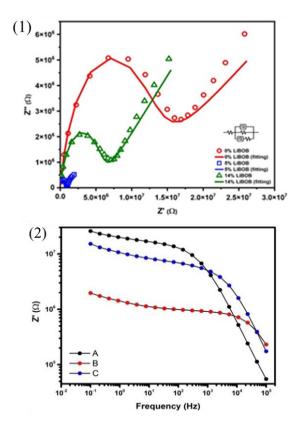


Figure 1. Nyquist curve (1) and Bode plot (2) SPE samples with variations in the addition of LiBOB: A) A-0% LiBOB, B). B-5% LiBOB and C). C-14% LiBOB

Moreover, conversely at the highest frequency of 100000 Hz, A-0% LiBOB had the slightest resistance than B-5% LiBOB and C-14% LiBOB. From Table 2, A-0% LiBOB had the highest conductivity value of 3.643 x 10⁻⁵ S/cm. However, the results of this study differed from those reported by Shanthi et al., (2018). The article produced a conductivity of 1.3 x10⁻³ S/cm, using a mixture of LiTFSI and LiNO₃ salts on the PVdF-HFP/SiO₂ polymer system with the Electrospinning method [10]. The combination of PVdF-HFP and PMMA with the addition of NaI reported by Tripathi et al., (2012) resulted in conductivity of 1.67 x 10^{-2} S/cm [9]. By comparing this research with previous studies, it can be concluded that the conductivity value was strongly influenced by the combination of electrolyte salts, combinations of polymer types, types of ceramic fillers, and solid polymer electrolyte production methods. The results of this conductivity analysis were strengthened by XRD, FTIR, SEM, and TGA analysis as in the following discussion.

Table 2. Sample specifications, Re value (electrolyteresistance) and conductivity

Sample	p(cm)	l(cm)	t(cm)	A(cm)	Re(ohm)	σ (S/cm)
A- 0% LiBOB	1	0,5	0.0208	0.0104	5,49E+04	3,643 x 10-5
B-5% LiBOB	1	0,5	0.0200	0.0100	2,31E+05	8,658 x 10-6
C-14% LiBOB	1	0,5	0.0230	0.0115	1,74E+05	1,149 x 10-5

 σ = conductivity, t= thickness, A= area, p = length, l = width dan Re = Electrolytic resistance (SPE)

3.2. X-ray Diffraction (XRD) Analysis

XRD patterns for various variations of the addition of LiBOB salt to SPE include A) A-0% LiBOB, B). B-5% LiBOB and C). C-14% LiBOB at room temperature is shown in Figure 2.

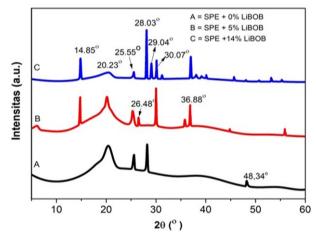


Figure 2. XRD spectra for A) A-0% LiBOB, B) B-5% LiBOB, and C) C-14% LiBOB

The amorphous or crystalline phase of a material can be observed by analyzing one or two diffraction pattern peaks. The relationship between the intensity of the XRD pattern and the degree of crystallinity was observed by Hodge et al. [19]. The increase in amorphous properties was characterized by a decrease in the intensity and loss of the XRD pattern [20]. The more amorphous the polymer, the higher the conductivity. In amorphous polymer matrices, charge transfer becomes more effective because free spaces allow ion movement to occur effectively than crystalline polymer matrices [3]. The semi-crystalline structure (coexistence of crystals) and amorphous mixtures for PVdF-HFP were observed at the peaks of the XRD pattern at angles of 20: 20.4° and 38° [9]. LiTFSI salt crystalline character can be marked peak XRD pattern at 20 angles 14.11°, 15.91°, 18.61°, 18.91°, and 21.41°. All peaks show that the crystalline character will be lost, and there was only one peak at a 2θ angle of 14.11° when the LiTFSI salt was dispersed in the polymer matrix [18]. In Figure 2A, the XRD peaks for A-0% LiBOB can be found at angles of 20: 20.23°, 25.55°, 28.03° and 48.34°. The addition of 5% LiBOB (Figure 2B) caused the formation of new peaks at angles of 20: 14,85°, 26.48°, 30.07° and the loss of peaks at angles of 2θ : 28.03° and 48.34°. This phenomenon indicated that a reaction had occurred with the added LiBOB. Assuming the amount of LiBOB salt added was proportional to the LiTFSI salt contained in the SPE, it caused new peaks with high intensity to appear at 28.03°, 29.04°, and many new peaks appeared with low intensity after an angle of 36.88° (Figure 2C). XRD analysis shows that an increase in the amount of LiBOB added led to a rise in crystalline properties characterized by the appearance of several new peaks at B-5% LiBOB and C-14% LiBOB. The minor peaks indicated that the A-0% LiBOB was the most amorphous among the other samples. As a result, the movement of Lithium ions in A-0% LiBOB wass more substantial than in other samples, as evidenced by the conductivity value of 3.643 x 10⁻⁵ S/cm.

3.3. Fourier Transform Infrared (FTIR) Analysis

The FTIR curve for A-0% LiBOB, B-5% LiBOB, and C-14% LiBOB at room temperature is shown in Figure 3.

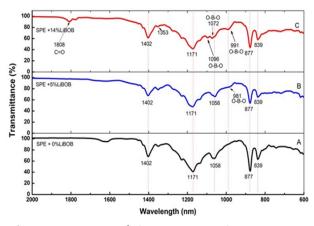


Figure 3. FTIR curve of A) A-0% LiBOB, B) B-5% LiBOB, and C) C-14% LiBOB

The vibrational bond at 874 cm⁻¹ is the absorption band in pure HFP PVDF, which shifted to a wavenumber of 877 cm⁻¹ due to the addition of LiTFSI salt. Pure LiTFSI absorption band at 842 cm⁻¹ and 1357 cm⁻¹ corresponded to N-CO-O symmetric stretching and SO₂ asymmetric stretching [21] experienced a shift to 1353 cm⁻¹ and 839 cm⁻¹, respectively are shown in Figure 3A. This confirmed the presence and occurrence of salt complexation with the polymer. In other words, the Lithium-ion from the LiBOB and LiTFSI electrolyte salts would bind to the PVdF HFP polymer compound as the polymer host. Assuming two or more compounds are mixed, the spectra peaks will shift due to physical interactions and chemical reactions [4]. The absorption band at wave number 1402 cm⁻¹ corresponded to -CF₂ stretching on PVDF-HFP [2]. The peak at 1171 cm⁻¹ is assigned to the symmetrical stretching mode CF₂ of PVDF-HFP, which had shifted due to adding salt. The addition of 5% LiBOB caused the appearance of an absorption band at wavenumber 981 cm⁻¹, which was B-O-B stretching. The addition of LiBOB to 14% would shift or eliminate the absorption band at a wavelength of 1058 cm⁻¹, shifting to 1072 cm⁻¹ and 1098 cm⁻¹, which is a stretching BOB group bond and a low-intensity peak appeared at 1808 cm⁻¹ as C=O bond. Based on the results of this FTIR analysis, it can be shown that there had been an interaction of LiBOB salts in the SPE system (PVDF-HFP, TiO₂, and LiTFSI).

3.4. Scanning Electron Microscope (SEM) Analysis

Analysis of the morphological structure using SEM was observed on the surface of the electrolyte membrane, as shown in Figure 4. The magnification used was 2500 times. Figure 4 shows a network of interconnected pores shaped like a wasp's nest. The pores formed have a diameter of \pm 2–6 mµ. Commercial separators used for lithium-ion battery cells generally have a pore size of < 1 mm [22]. The pores in the SPE were a prerequisite for lithium-ion transport during the cycle. The addition of LiBOB salt in the SPE system will affect the condition of the pores formed.

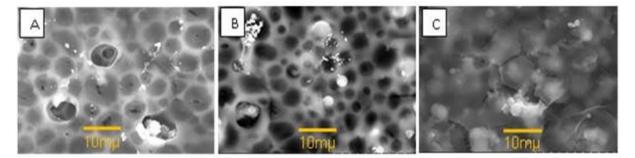


Figure 4. SEM observations on A) A-0% LiBOB, B) B-5% LiBOB, and C) C-14% LiBOB

From Figure 4, the B-5% LiBOB would change the pore size to be smaller and the distance between the pores to be longer. In addition, it could eliminate the arrangement of pores that are arranged in layers in the polymer electrolyte membrane. In contrast, the condition of the pores arranged in layers like this was indispensable because it was advantageous for storing liquid electrolytes and would even facilitate the movement of ions to be more effective.

Energy Dispersive Spectroscopy (EDS) was used to determine the elemental composition B, C, O, Ti in the SPE sample with 14.5% LiBOB (Sample C). The result shows that the unit elements B, C, O, Ti were dispersed uniformly in SPE, as shown in Table 3 and Figure 5.

Table 3. EDX analysis of C-14.5% LiBOB

Element	Spec-1	Spec-2	Spec-3	Spec-4	Spec-5	Spec-6	Spec-7	Spec-8
BK	10.04	10.94	11.26	10.58	15.19	13.03	9.97	10.02
CK	65.98	62.43	67.15	68.64	58.83	66.03	69.77	71.13
OK	5.21	4.58	1.97	1.59	1.46	1.32	2.1	1.62
FK	18.34	20.1	18.05	18.95	22.4	19.07	18.06	17.17
TiK	0.42	1.95	1.58	0.24	2.12	0.55	0.1	0.06

This EDS analysis can indicate all the constituent components of SPE have been mixed evenly. The pore morphology of the C-14.5% LiBOB was blocked with the addition of excess LiBOB due to agglomeration (Figure 4C). Thus, A-0% LiBOB was expected to facilitate the rapid transport of Lithium ions because it has a larger pore size, shorter inter-pore distance, and a layered pore arrangement in the SPE.

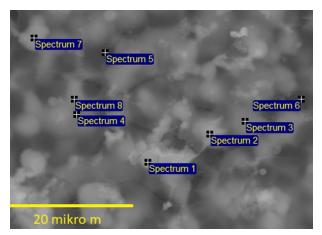


Figure 5. Distribution of SPE constituent elements in a sample of C-14.5% LiBOB

3.5. Heat Analysis using TGA (Thermogravimetric Analysis)

TGA was used to determine the heat stability of the SPE. The TGA result of SPE samples containing PVDF-HFP/TiO₂/LiTFSI with variations in the addition of LiBOB: A) A-0% LiBOB, B) B-5% LiBOB, and C) C-14% LiBOB is presented in Figure 6. Sample observations were carried out at a temperature ranging from 100 to 400°C. The LiTFSI salt in the polymer can absorb water from the outside [23]; consequently, the weight loss in A-0% LiBOB was lower than others. The A-0% LiBOB experienced a 10.6 % weight loss in a temperature range from 161.8-319.2°C. According to the reference, the PVDF-HFP and LiTFSI compounds have decomposition temperatures of ~465°C and 340°C, respectively [21]. Consequently, the components that undergo decomposition may only be water molecules or solvents used. The B-5% LiBOB sample showed a 34.06% weight loss in the range of 112.5-319.2°C because the decomposition temperature of LiBOB occurs at >290°C [24].

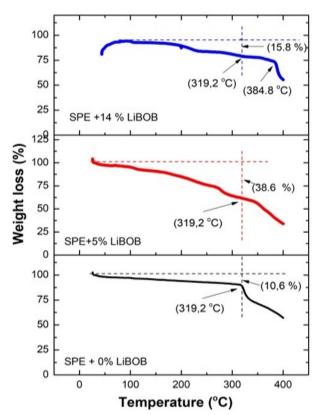


Figure 6. Thermal analysis on A-0% LiBOB, B-5% LiBOB, and C-14% LiBOB

An increase in the amount of LiBOB equal to the amount of LiTFSI (C-14% LiBOB) decreased the weight loss to 15.8% in the temperature range of 194.3–319.2°C. This decrease in weight loss was probably due to the gradual decomposition process in the temperature range of 194.3–319.2°C. The C-14% LiBOB showed a drastic reduction in thermal stability at 384.8°C. Thermal decomposition of PVdF HFP pristine occurs at ~465°C, LiBOB occurs at >290°C, and LiTFSI occurs at ~340°C [21]. From the discussion above, it can be concluded that the addition of LiBOB affected the heat stability of SPE containing LiTFSI salt.

3.6. Cyclic Voltammetry (CV) Analysis

provides Cyclic voltammetry (CV) analysis information about the current and voltage of the battery cells. The electrochemical process of battery cells when charging and discharging is described in a CV curve. Figure 7 shows the results of cyclic voltammetry observations on a half cell LiTiO₂/Li battery using SPE A-0% LiBOB and 5% LiBOB samples. Based on CV results, the charging (oxidation) and discharging (reduction) processes of the battery cells were obtained for the A-0% LiBOB and the B-5% LiBOB. Both samples underwent oxidation and reduction processes. From Figure 7 and Table 4, it can be seen that the oxidation peak (Epa) and reduction peak (Epc) of the two samples almost have the exact sizes; however, the current measured in A-0% LiBOB was higher than in B-5% LiBOB. Theoretically, the smaller the value V, the better the ion reversibility. In this study, sample A-0% LiBOB with V= 0,576 had better reversibility properties than sample B-5% LiBOB with V = 0.64.

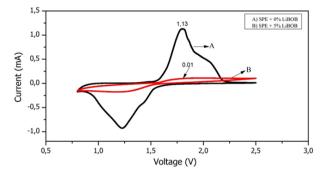


Figure 7. Cyclic Voltammetry (CV) analysis on SPE A-0% LiBOB and B-5% LiBOB

Table 4. Current and voltage values for samples A-0%LiBOB and B-5% LiBOB based on CV results

Sample ·	Currer	it (mA)	Volta	ΔV	
	Oxidation	Reduction	Oxidation	Reduction	Δv
A-0% LiBOB	1.133	-0.953	1.801	1.225	0.576
B-5% LiBOB	0.127	-0.183	1.870	1.224	0.646

4. Conclusion

LiBOB has been added to the manufacture of SPE based on PVDF-HFP/TiO₂/LiTFSI through the solution casting method. Based on the results of the EIS analysis, the value of ion conductivity decreased from 3.643×10^{-5} S/cm to 8.658×10^{-6} S/cm. These results have been

supported by the results of XRD analysis, where the SPE samples with the addition of LiBOB (B-5% LiBOB and C-14% LiBOB) increased crystalline properties. The SEM analysis showed that the pore size was partially reduced, the distance between the pores became longer, and the pore closure occurred due to agglomeration. The results of the FTIR analysis also showed a shift in the absorption band, which indicated that there had been an interaction of LiBOB salts in the PVDF-HFP/LiTFSI/TiO₂ system. The addition of LiBOB also affected the heat stability of SPEs containing LiTFSI salts. Based on CV analysis, the addition of LiBOB in the SPE system could decrease the reversibility of the ion and the current.

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