

## Conference Paper

# Preparation and Characterisation of PVdF-LiBOB-Based Solid Polymer Electrolyte

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**Abstract** Electrolyte plays a key role in lithium-ion battery system. Safety and reliability factor was the main background of the development of solid polymer electrolyte as a substitute the conventional electrolyte in liquid form. Preparation and characterisation of a polymer electrolyte system based on lithium bis(oxalato) borate or LiBOB salt and PVdF as the host matrix has been performed. LiBOB salt and PVdF polymer were dissolved in DMAC solvent followed by solid polymer electrolyte forming by means of doctor blade method. The membranes obtained were characterised by FT-IR, XRD, and EIS. It was shown that the electrolyte exhibited higher room ionic conductivity with the increase of salt concentration, with highest conductivity value of  $1.22 \times 10^{-6} \text{ Scm}^{-1}$  for 70% LiBOB concentration.

**Keywords:** doctor blade, polymer electrolyte, LiBOB, PVdF

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## 1. Introduction

The necessity of the sources of renewable energy is increasing with the development of portable electronic gadgets as well as electrical vehicles. Rechargeable lithium-ion battery or secondary battery has taken many attention because its high energy density and long life cycle [1]. Electrolyte contributes greatly in a lithium-ion battery system in terms of ion transport. Liquid electrolyte commonly used by lithium-ion batteries consists of electrolyte salts such as lithium hexafluorophosphate ( $\text{LiPF}_6$ ) and carbonate solvents such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC).  $\text{LiPF}_6$  has conductivity as high as  $> 10^{-2} \text{ Scm}^{-1}$  in room temperature, but low thermal stability at high temperature; [2] its decomposition yields HF that has destructive properties towards battery cathode cells [3].

Since its invention by Lischka et.al, [4] new electrolyte salt LiBOB has been developed as  $\text{LiPF}_6$  substitute [5]. Conductivity of LiBOB is relatively lower than  $\text{LiPF}_6$  (approximately  $6 \times 10^{-3} \text{ Scm}^{-1}$ ) but it has better thermal stability as well as capacity retention compared to  $\text{LiPF}_6$  [6,7]. Lithium-ion battery requires reliability at high temperature such as for electric vehicle and oil and gas application, therefore safety issue is considered an important factor. Safety and reliability factor was the main background of the development of solid polymer electrolyte as a substitute the conventional electrolyte in liquid form. Batteries with liquid electrolyte in carbonate

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solvent is potentially explosive because the materials are volatile and easily flammable at temperature higher than 60°C, therefore polymer electrolyte has been widely developed as a safer alternative [8].

Polymer electrolyte was widely developed to obtain more compact and lightweight lithium-ion battery, but complied with safety requirements [9]. PVdF has some benefits compared to other polymers, e. g higher dipole moment and dielectric constant, which are important factors for lithium salt ionization [10]. Besides, PVdF is also advantageous in terms of mechanical strength, electrode-electrolyte interaction, good porosity control in multiple polymer/solvent system, and high anodic stability due to -C-F-bonds which has strong electron-withdrawing properties [11]. In its development, there are three kinds of polymer electrolyte: dry solid polymer electrolyte, gel polymer electrolyte, and porous polymer electrolyte [12]. Dry solid polymer electrolyte system was chosen for this experiment due to its simplicity in structure and higher mechanical strength compared to gel polymer electrolyte [13]. From the characteristics of electrolyte salts and polymers in lithium-ion battery system, PVdF and LiBOB were chosen as polymer host and carrier, respectively. The purpose of this experiment is to obtain PVdF and LiBOB-based solid polymer electrolyte and to study the effect of LiBOB salt addition in solid polymer electrolyte system.

## 2. Experimental Method

LiBOB salt was synthesized using solid state reaction according Wigayati, et.al. [14]. Precursor All materials were obtained from Merck Millipore and Sigma Aldrich, with purity of > 98%. PVdF was dissolved in DMAC and mixed at 70°C temperature. LiBOB salt with varied ratio was then added into the solution. PVdF-LiBOB solution was casted on a glass substrate using doctor blade technique with 400 μm thickness and dried in room temperature with low humidity.

The formed membrane was dried in the oven to evaporate excess solvent. The phase and crystal structure of polymer electrolyte was observed using X-Ray Diffraction (XRD) Rigaku type Smartlab under Cu K $\alpha$  radiation within 2 $\theta$  range of 0-80°. Functional groups and intermolecular binding were observed using Fourier Transform Infra-Red (FT-IR) Thermoscientific type Nicolet iS-10 with attenuated total reflectance (ATR) method, operated at wave number range of 4000 – 600 cm<sup>-1</sup>.

Impedance test of polymer electrolyte was performed using Hioki LCR HiTester type 3522-50. The measurement of bulk resistance (R<sub>b</sub>) can be determined from Cole-Cole plot obtained from impedance test. Hence, the conductivity ( $\sigma$ ) was calculated using simple formula  $\sigma = L/(R_b \times A)$ , with L and A are sample thickness and surface area of the stainless steel plate, respectively.

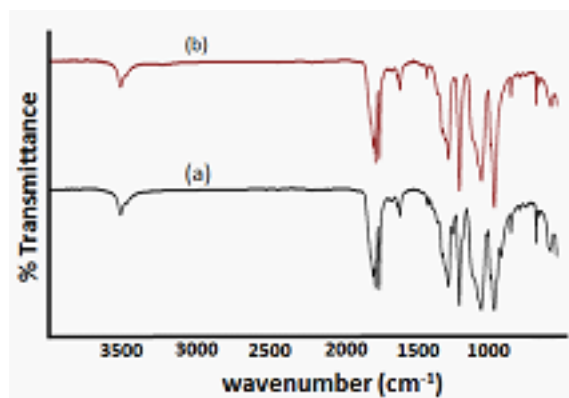


Figure 1: FT-IR characterisation of (a) commercial, and (b) synthesized LiBOB.

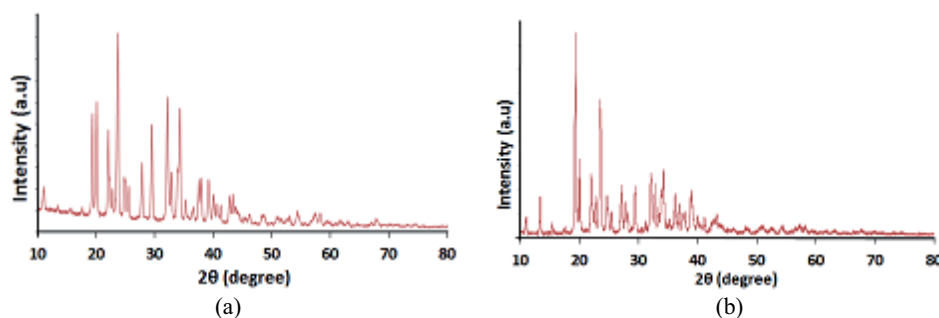


Figure 2: XRD characterisation of (a) commercial and (b) synthesized LiBOB.

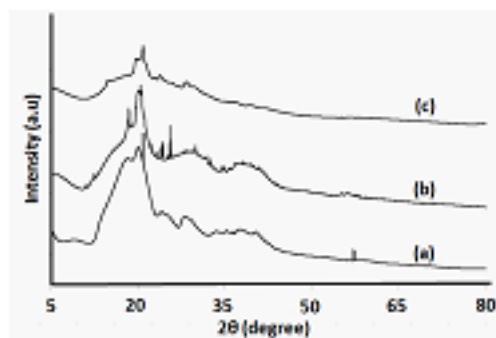
## 3. Results and Discussion

### 3.1. Characterisation of synthesized LiBOB

Crystal structure, composition, and functional groups of synthesized LiBOB were presented in FT-IR and XRD analysis results at Fig. 1 and 2. It was shown in Fig. 1 that functional groups formed in synthesized LiBOB were close in reference to commercial LiBOB salt. [15]. Vibration peak at wave number 1750, 1640, and 1442  $\text{cm}^{-1}$  indicate C=O stretch, COO asymmetric stretch, and COO symmetric stretch, respectively. Fingerprint region of LiBOB compound was characterised by vibration peak at wave number 1372, 1297, 1070, and 982  $\text{cm}^{-1}$ .

These peaks represented B-O stretch, C-O-B-O-C stretch, O-B-O symmetric stretch and O-B-O asymmetric stretch, respectively. Vibration peak at wave number 3513  $\text{cm}^{-1}$  represented O-H stretch, indicating that hydrate crystal was formed in LiBOB hydrate phase. The appearance of this phase was also observed in XRD analysis result as shown in Fig. 2.

XRD diffraction pattern was illustrated in Fig. 2(a) for commercial LiBOB and Fig. 2(b) for synthesized LiBOB. Both figure of peak diffraction analysis exhibited LiBOB and LiBOB hydrate phase. For commercial LiBOB in Fig. 2(a), LiBOB phase (ICDD/PDF4 #00-056-0139) [16] was indicated by three strongest lines at d-spacing 2.78, 4.42, and 4.58 Å. LiBOB hydrate phase (ICDD/PDF4 # 01-073-9447)[16] was indicated by three strongest lines at d-spacing 2.62, 4.03, and 3.20 Å.



**Figure 3:** X-Ray diffraction spectra for (a) 30%, (b) 50%, and (c) 70% LiBOB concentration.

For synthesized LiBOB in Fig. 2(b), LiBOB phase (ICDD/PDF4 #00-056-0139) [16] was indicated by three strongest lines at d-spacing 4.57, 2.31, and 3.28 Å. LiBOB hydrate phase (ICDD/PDF4 # 01-073-9447) [16] was indicated by three strongest lines at d-spacing 3.75, 2.79, and 4.04 Å.

### 3.2. XRD analysis

X-Ray diffractograms of solid polymer electrolyte sample with 30%, 50%, and 70% addition of LiBOB were illustrated at Fig. 5.

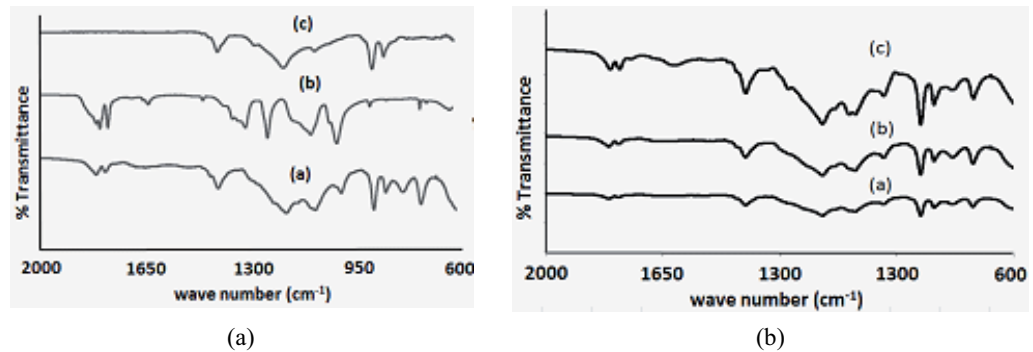
Diffraction peak analysis showed that  $\beta$ -PVdF phase which supposedly appeared at  $2\theta = 20.9^\circ$  did not appear because LiBOB crystal phase was more dominant at  $2\theta$  range of  $5^\circ$  to  $45^\circ$ . This showed that LiBOB particle was distributed evenly within PVdF matrix as polymer host [17].

### 3.3. FT-IR analysis

PVdF and LiBOB functional groups within solid polymer electrolyte system was presented at Fig. 6. It was seen that solid polymer electrolyte spectrum for 50% LiBOB concentration was a combination of functional groups as well as fingerprints of pure PVdF and LiBOB. Vibration peak at wavenumber 1810, 1633, 882, and 723  $\text{cm}^{-1}$  were typical fingerprint of LiBOB compound, which represented vibration of C=O oscillation, C-O-O asymmetric stretch, O-B-O asymmetric stretch, and C-O-O bending vibration, respectively. Vibration peak of PVdF fingerprints were also seen at wavenumber 1403  $\text{cm}^{-1}$  which was  $\text{CH}_2$  scissoring, and C-F stretch at 1074  $\text{cm}^{-1}$ . There were also typical vibration peak of  $\beta$ -PVdF phase at 838  $\text{cm}^{-1}$ , which were  $\text{CH}_2$  rocking and asymmetric stretch of  $\text{CF}_2$  [18].

FT-IR spectrum comparison of PVdF-LiBOB solid polymer electrolyte system with LiBOB concentration of 30%, 50%, and 70% was presented at Fig. 7. Vibration peak showing C-O-O asymmetric stretch from LiBOB at wave number 1633  $\text{cm}^{-1}$  was seen more clearly with more LiBOB concentration.

Conversely,  $\text{CH}_2$  in-plane bending or rocking which was distinctive fingerprint of  $\beta$ -PVdF phase was even more reduced. This suggested that LiBOB particle was distributed



**Figure 4:** FT-IR spectrum of (a) pure PVdF, pure LiBOB, and PVdF-LiBOB membrane, and (b) PVdF-LiBOB membrane with LiBOB concentration of 70%, 50%, and 30%.

LiBOB content, %	Conductivity, Scm <sup>-1</sup>
30	$2.66 \times 10^{-9}$
50	$3.96 \times 10^{-8}$
70	$1.22 \times 10^{-6}$

TABLE 1: Room temperature conductivity of PVdF-LiBOB solid polymer electrolyte.

evenly within solid polymer electrolyte system, as was also shown in the SEM scan results of the membrane.

### 3.4. Electrochemical Impedance Spectroscopy analysis

The ionic conductivity of PVdF-LiBOB solid polymer electrolyte system was observed using electrochemical impedance spectroscopy (EIS). Bulk resistivity value obtained from the Cole-Cole plot was used to calculate the room temperature conductivity of PVdF-LiBOB solid polymer electrolyte, which result was presented on Table 1.

Impedance test exhibited increasing conductivity on addition of LiBOB salt. At 30% salt concentration, LiBOB particle functioning as conductor was agglomerated within polymer matrix as shown at Fig. 4. The highest conductivity at 70% salt concentration was affected by higher amount of LiBOB particle distributed within PVdF polymer matrix. Studies performed by Xi et.al [19] on characterisation of PVdF-LiClO<sub>4</sub>-based solid polymer electrolyte in propylene carbonate (PC) solvent showed ionic conductivity as high as  $1 \times 10^{-5} \text{ Scm}^{-1}$  at room temperature. Stephan and Nahm [20] also reported similar result for PVdF-LiPF<sub>6</sub>-based solid polymer electrolyte system. PEO-LiClO<sub>4</sub>-based solid polymer electrolyte system showed lower conductivity, i.e  $1 \times 10^{-8} \text{ Scm}^{-1}$ .

## 4. Conclusion

PVdF-LiBOB-based solid polymer electrolyte system has been synthesized and characterised. Solid polymer electrolyte synthesized from PVdF polymer host and LiBOB salt filler using doctor blade method was evenly distributed throughout the surface as well as membrane layer. Even though the distribution of LiBOB particle was relatively homogenous within PVdF matrix as polymer host, but at low salt concentration there

was a possibility of agglomeration. The ionic conductivity of the solid polymer electrolyte system increased with addition of LiBOB salt. The ionic conductivity of solid polymer electrolyte system with 30%, 50%, and 70% salt concentration was  $2.66 \times 10^{-9}$ ,  $3.96 \times 10^{-8}$ , dan  $1.22 \times 10^{-6} \text{ Scm}^{-1}$  respectively, at room temperature (25°C). The ionic conductivity of this solid polymer electrolyte system can be enhanced with addition of filler and plasticiser.

## 5. Acknowledgement

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