

## Synthesis and Characterization of PVDF-LiBOB Electrolyte Membrane with ZrO<sub>2</sub> as Additives

Etty Marti Wigayati<sup>1</sup>, Moh Rosyid Ridho<sup>1</sup>, Achmad Subhan<sup>1</sup>, Ibrahim Purawardi<sup>1</sup>

<sup>1</sup>Research Center for Physics, Indonesian Institute of Sciences  
Kawasan Puspiptek Serpong Gd. 442, Tangerang Selatan – Banten

\*Corresponding Author: [etty001@lipi.go.id](mailto:etty001@lipi.go.id)

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### ABSTRACT

The electrolyte membrane serves as ions medium transport and as a separator between the anode and cathode in lithium ion battery. The polymer used for the electrolyte membrane must have sufficiently high mechanical strength to endure the pressure between the anode and cathode, a thin size and has a chemical and thermal stability.

Polymer electrolyte membrane of lithium bisoxalate Borate (LiBOB) salt with PVdF as matrix polymer and the additive namely ZrO<sub>2</sub> has been fabricated. The method used was a doctor blade. The concentration of the additive was varied. The membranes were characterized using FT-IR, XRD, SEM and EIS. XRD analysis showed that the crystallinity index increased by the addition of ZrO<sub>2</sub>. The presence of functional groups in between lithium salts and polymer interaction investigated by FTIR analysis. The morphology of the membrane surface was identified by SEM analysis. SEM image and mapping showed the morphology of the membrane have typical porous layer. The electrical conductivity increased by the additions of ZrO<sub>2</sub>.

Key word: additive, cristalinity index, electrical conductivity, morphology

### INTRODUCTION

Electrolytes play an important role in the lithium-ion battery system for the transfer of ions. Lithium-ion batteries typically use a liquid electrolyte consisting of a lithium hexafluorophosphate (LiPF<sub>6</sub>) and carbonate solvents such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) or diethyl carbonate (DEC). LiPF<sub>6</sub> has conductivity higher than 10<sup>-2</sup> Scm<sup>-1</sup> at room temperature, but low thermal stability at high temperatures [1-2]. LiPF<sub>6</sub> even decomposed into LiF and PF<sub>5</sub> then react with H<sub>2</sub>O to form HF, which is destructive to the battery cathode cells [1,3]. LiBOB ((lithiumbis(oxalato)borate)) is a lithium salt which is proposed to be used as electrolyte materials in lithium ion batteries, replace LiPF<sub>6</sub> because it has a stable SEI capability, a wide potential window. It has solubility in carbonate solvents such as: EC, DMC, DEC, high electrical conductivity and good cycling. In organic solvents LiBOB provides superior thermal stability than LiPF<sub>6</sub>. LiBOB crystallinity is also more stable than LiPF<sub>6</sub>.

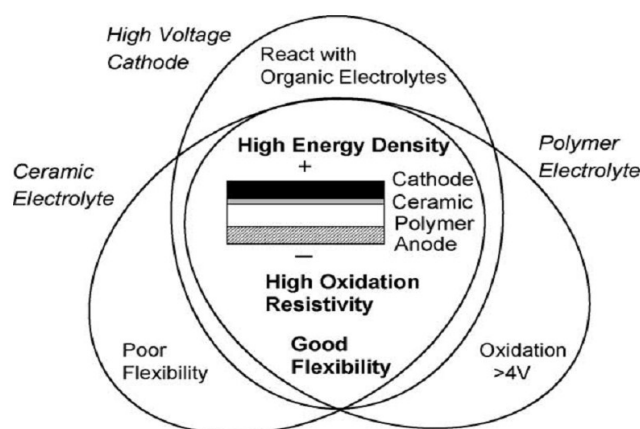
Lithium ion batteries require durability at high temperatures, such as electric vehicles or gas exploration so the battery safety is a factor that must be considered. Batteries with liquid electrolyte containing carbonate solvents have the potential to cause an explosion because it is volatile and burns at high temperatures (> 60°C), therefore the polymer electrolyte developed as a safer alternative [4].

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The polymer electrolyte is more developed to obtain lithium-ion batteries that are thinner, lighter, but it has to meet safety qualities [5]. Several studies like PEO addition have investigated a wide range of polymers to be used as the host polymer in polymer electrolyte systems such as polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA), polyacrylonitrile (PAN), and polyvinylidene fluoride (PVdF). PVdF has advantages over other polymers such as dipole moments and high dielectric constant, which is important for the ionization of lithium salt [6]. In addition, the PVdF is also superior in terms of mechanical strength, the interaction of electrode-electrolyte, good control for porosity in the doubles system solvent/polymer, also the high stability of the anodic due to the presence of functional groups C-F which has the property of attracting strong electron [7]. Safety and durability makes the solid polymer electrolyte started more developed to replace conventional electrolyte in liquid form.

There are three types of polymer electrolyte: solid polymer electrolyte, gel polymer electrolyte, and porous solid polymer electrolyte [8-9]. Solid polymer electrolyte has a higher mechanical strength than gel polymer electrolyte.

Electrolyte membrane is a matrical solid electrolyte which is a solid solution of alkali metals in the polymer [10]. Electrolyte membrane has the advantages such as the ion conductivity and the energy density is high enough, leak-proof, solvent-free, have electrochemical stability, easily manufactured, and light. Membrane electrolyte in lithium ion battery has a dual function as a medium transport of ions (replacement electrolyte solution) and as a separator between the cathode and the anode. In the later development the required electrolyte membrane has the characteristics: high conductivity, mechanically strong, thermal stability and can be produced inexpensively. Various polymers have been used for the electrolyte membrane, for example PVdF, PVA, cellulose acetate, polyacrylonitrile-methyl methacrylate P (AN-MMA).



**Figure 1.** Schematic of “Ceramic/polymer composite concept [13]

ZrO<sub>2</sub> has excellent thermodynamic properties of ZrO<sub>2</sub>, high ionic conductivity, strong and stable [11-12]. Schematically, lithium ion polymer was depicted in Figure 1.

In this research, the solid polymer electrolyte (SPE) membrane has been prepared. Composites made from LiBOB as active material and PVdF polymer as a matrix. ZrO<sub>2</sub> was added to strengthen the mechanical properties and increase the electrical conductivity. The SPE will be used for the electrolyte in lithium batteries.

## EXPERIMENT

### Chemicals and instrumentation

PVdF was purchased from Sigma Aldrich with purity > 98% and a molecular weight > 180,000 (GPC). Solvent N,N-dimethylacetamide (DMAC) were purchased from Merck with purity > 99%. ZrO<sub>2</sub> was obtained from Kanto Chemical Co. EC / DEC were obtained from Merck with purity > 98%, and LiBOB salt was synthesized using solid state reaction according to Wigayati, et.al.[19,20].

The process was conducted by mixing for membrane preparation was used a magnetic stirrer on hotplate IKA C- MAG HS-7. The crystalline structures and crystallinity were analyzed using XRD Rigaku SmartLab type with Cu K $\alpha$  radiation in the range of  $2\theta = 0-80^\circ$  then the results are analyzed using the software PDXL. The functional groups were analyzed using FT-IR Thermoscientific type Nicolet iS-10 machine by attenuated total reflectance (ATR) method in the range of wave number 4000-600 cm<sup>-1</sup>. The surface morphology of membrane characterization using Scanning Electron Microscope (SEM) Hitachi SU-350 types operated at 10-20 kV acceleration voltage. The electrical conductivity was analyzed using Hioki 3522-50 LCR HiTESTER type.

### Procedure reaction

PVdF dissolved in DMAC and stirred using a magnetic stirrer with a speed of 250 rpm was put on a hot plate at a temperature of 50°C. LiBOB salt mixed in EC and DEC until dissolved. Then two solutions were mixed together and added by ZrO<sub>2</sub>. Obtained solution was stirred continuously until the mixture becomes homogeneous viscous liquid appearance. The solutions were cast on to a glass substrate plates using doctor blade methods with films thickness of 100  $\mu\text{m}$ , and allowed to evaporate slowly at room temperature. The polymer electrolyte membrane composition showed in Table 1.

**Table 1.** Composition of the polymer electrolyte membrane (in percent by weight)

Sample	PVDF	EC	DEC	LiBOB	ZrO <sub>2</sub>
PEM 1	30	32.5	32.5	5	0
PEM 2	30	31.25	31.25	5	2.5
PEM 3	30	30	30	5	5
PEM 4	30	28.75	28.75	5	7.5

### Characterization of PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane

Characterization of surface morphology of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane was performed by a scanning electron microscope (SEM). Phase and the crystal structure of the polymer electrolyte membrane were observed by X-ray diffraction analysis (XRD). Samples were scanned using XRD. Analysis of the functional groups and the bond between molecules was done using Fourier Transform Infra-Red spectroscopy (FT-IR).

Test impedance the polymer electrolyte membrane sheet made by electrochemical impedance spectroscopy (EIS). The samples were placed between stainless steel plates in an area of 9.64 mm<sup>2</sup> and AC current is applied in the frequency range of 0.5 Hz to 100,000 Hz. Conductivity ( $\sigma$ ) can be calculated using the formula :

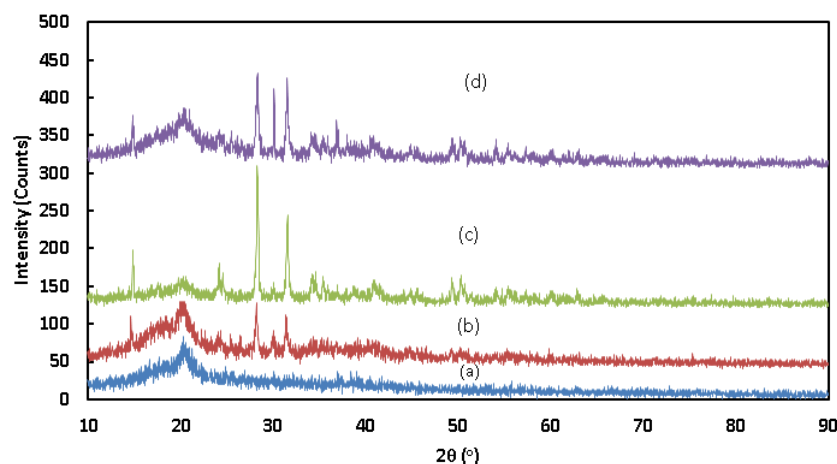
$$\sigma = \frac{L}{R_b \times A} \quad (1)$$

where  $L$  and  $A$  are each the polymer electrolyte membrane thickness and sample size respectively, while the bulk resistance  $R_b$  is obtained from Cole-Cole plot impedance test results.

## RESULT AND DISCUSSION

### XRD analysis

The resulted crystal structure and composition of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane shown in Figure 2 XRD analysis.



**Figure 2.** The diffraction patterns the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane with ZrO<sub>2</sub> (a) 0%, (b) 2.5%, (c) 5% and (d) 7.5%.

The formed phase is shown in Figure 2(a). The results of the analysis of diffraction peaks indicating the presence of  $\beta$ -PVdF (CF<sub>2</sub>CH<sub>2</sub>)<sub>n</sub> phase of ICDD (PDF-4+2015 RDB) DB card number 00-061-1404, at the height of the  $2\theta = 20.85$ ,  $36.72$  and  $41.45$ , as well as on the hkl plane each peaks (2,0,0), (0,0,1) and (2,0,1). LiBOB phase does not appear because in the sample PEM 1 the PVdF is more dominant than LiBOB particles, so the detected phase is PVdF.

The sample PEM 2 results phases Baddeleyite syn (ZrO<sub>2</sub>), ICDD (PDF-4 + 2015 RDB) DB card number 01-083-0940 and LiBOB hydrate (LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) by ICDD (PDF-4+2015 RDB) DB card number 01-073-9447, the diffraction peaks at  $2\theta = 20.22$ ,  $28.20$  and  $31.48$  and the hkl plane at each peaks (0,2,1), (4,1, 1) and (1,1,1).

The sample PEM 3 provides phases syn baddeleyite syn (ZrO<sub>2</sub>) with a percentage of 84% ICDD (PDF-4+2015 RDB) DB card number 01-083-0944; Tazheranite, syn (ZrO<sub>2</sub>) by ICDD (PDF-4+2015 RDB) DB card number 00-049-1642 and LiBOB hydrate (LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) by ICDD (PDF-4+2015 RDB) DB card number 01-073-9447 the height of the diffraction peaks at  $2\theta = 20.53$ ;  $28.31$  and  $31.49$ , as well as the hkl plane at each peaks (0,2,1), (1,1, -1) and ( 1,1,1).

The sample PEM 4, the phases formed is Zirconium Oxide (ZrO<sub>2</sub>) by ICDD (PDF-4+2015 RDB) DB card number 04-005-4478; Baddeleyite, syn (ZrO<sub>2</sub>) by ICDD (PDF-4+2015 RDB) DB card number 00-036-0420 and LiBOB hydrate (LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) by ICDD (PDF-4+2015 RDB) DB card number 01-073-9447, the height of the diffraction angle at  $2\theta = 20.34$ ,  $28.29$  and  $31.54$ , as well as the hkl plane at each peaks (4,0,0), (4,3,1) and (1, 1.1). At  $2\theta = 36.93$  a new peak represents the LiBOB hydrate (LiB (C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) phase.

From this analysis ZrO<sub>2</sub> is metal therefore it appears as dominant phase in the diffraction pattern, while the LiBOB phase appears in the form LiBOB hydrate because the

hygroscopic properties of LiBOB was binding with the water vapor in the air. Crystallinity index of the polymer electrolyte membrane do by peak height method [14]. Crystallinity indexes (CI) were calculated using the formula:

$$CI = \frac{(I_{\max} - I_{\min})}{I_{\max}} \quad (2)$$

where  $I_{\max}$  = highest intensity on the crystal diffraction peak and  $I_{\min}$  = lowest intensity in the valley crystal diffraction.

Calculation results are displayed in Table 2. From the analysis it appears that the crystallinity index of the polymer electrolyte membrane increases with the addition of  $ZrO_2$ , due to the  $ZrO_2$  is metal.

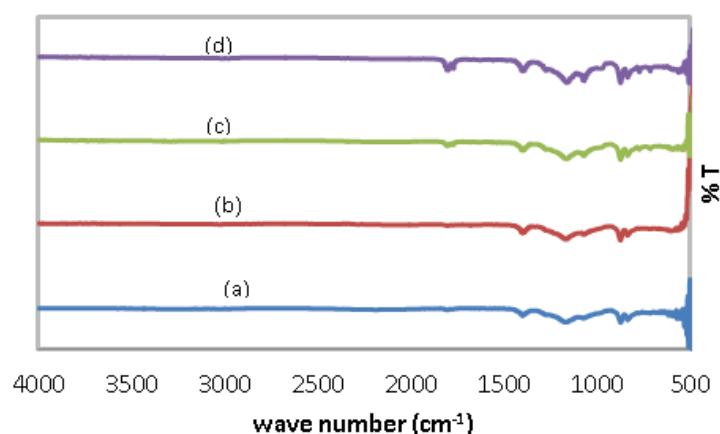
**Table 2.** The calculation results of crystallinity index

Sample	Crystallinity index (%)
CPE1	77.23
CPE2	94
CPE3	98.50
CPE4	96.08

### FTIR analysis

Figure 3 is an FT-IR spectrum, which showed the presence of functional groups PVdF and LiBOB appearing on the polymer electrolyte membrane sheet. The peaks of the wave number  $1807\text{ cm}^{-1}$ ,  $1777\text{ cm}^{-1}$ ,  $1071\text{ cm}^{-1}$  and  $876\text{ cm}^{-1}$ , is a fingerprint typical compound LiBOB, each of which showed the vibration of the oscillation C=O, C-O-O strain asymmetric O-B-O asymmetrical strain, and C-O-O buckling vibration.

The PVdF polymer fingerprint peak also appears at wave number  $1403\text{ cm}^{-1}$ , which  $CH_2$  cut out and C-F strain at wave number  $1074\text{ cm}^{-1}$ . Also visible fingerprint peaks typical  $\beta$ -PVdF phase at wave number  $838\text{ cm}^{-1}$ , the  $CH_2$  wobble, strain asymmetric of  $CF_2$  [15].  $CH_2$  in-plane bending is the characteristic fingerprints vibration of phase  $\beta$ -PVdF. The wave number of  $714\text{ cm}^{-1}$  and  $640\text{ cm}^{-1}$  is from  $ZrO_2$ .



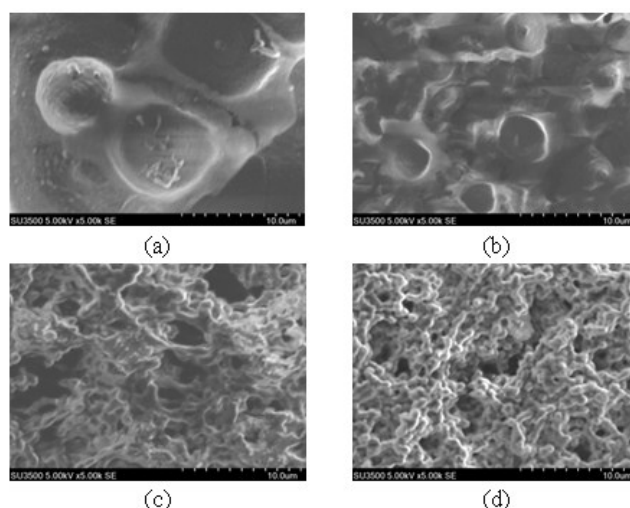
**Figure 3.** FTIR spectra of the sample PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane by the addition of ZrO<sub>2</sub> (a) 0%, ZrO<sub>2</sub> (b) 2.5% ZrO<sub>2</sub> (c) 5%, ZrO<sub>2</sub> (d) 7.5%

### SEM analysis

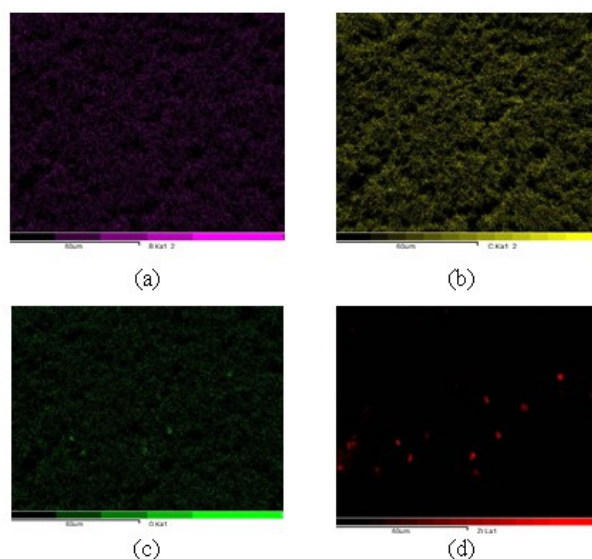
The polymer electrolyte membrane morphology showed in Figure 4. The Figure 4 is SEM analysis result was taken at 5000x magnification. From these images it appears that LiBOB particles are spread evenly throughout the matrix layer PVdF (Figure 4a). By the addition of ZrO<sub>2</sub> particles it grows more dense and homogeneous, ZrO<sub>2</sub> particles filling the space between the PVdF-LiBOB. Figure 5 shows the corresponding Energy Dispersive Spectroscopy (EDS) compositional mapping of the elements B, C, O, Zr in the polymer electrolyte membrane sample by addition of 7.5% ZrO<sub>2</sub>, indicating that the elements B, C, O, Zr units uniformly dispersed in the polymer electrolyte membrane.

The addition of ZrO<sub>2</sub> nanoparticles are dispersed homogeneously into the polymer matrix resulting in bonding between particles in the polymer chain bonded strongly with each other to form a membrane. The presence of nanoparticles dispersed between polymer chains inhibits reconstruction of intercellular polymer chains into crystalline form. When the temperature returns to room temperature, the polymer chain remains in the random or amorphous phase. With the survival of the amorphous state at low temperatures, the polymer conductivity will remain high at low temperatures [16]. In the sample by addition of ZrO<sub>2</sub> 7.5%, it appears that morphology has a good shape with very uniform polymer bonds. LiBOB is spread evenly and blends well into the polymer matrix. This illustrates that LiBOB is completely dissolved in the polymer matrix and ZrO<sub>2</sub>. So ZrO<sub>2</sub> as a dispersant occurs well.





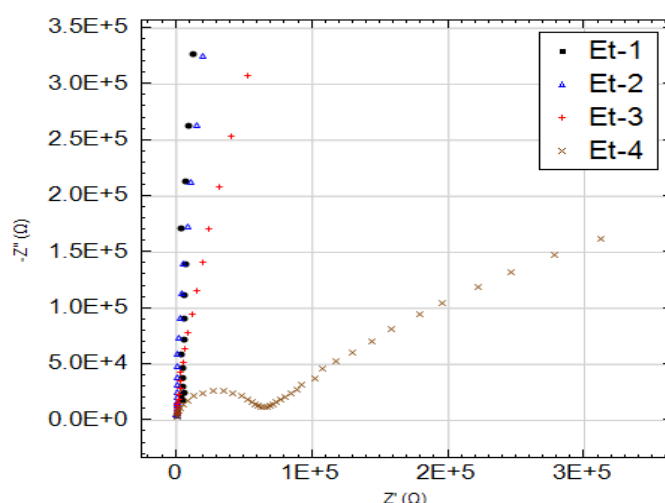
**Figure 4.** SEM picture of the surface of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane with variations of ZrO<sub>2</sub> (a) 0%; (B) 2.5%; (C) 5% and (d) 7.5%



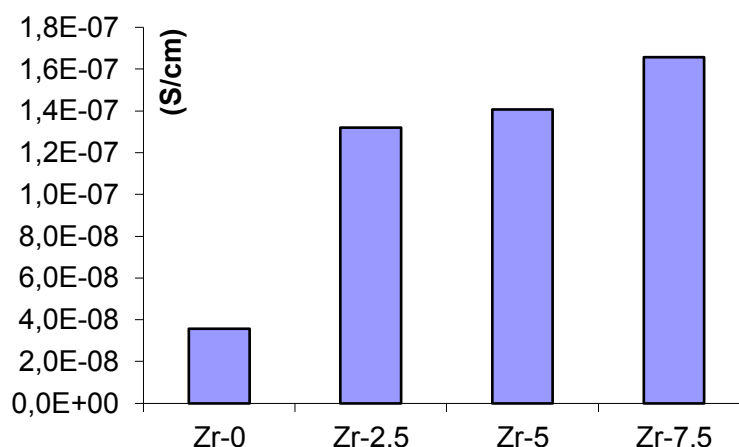
**Figure 5.** The results of the EDS analysis of mapping the elements (a) boron, (c) carbon, (o) oxygen and (d) Zr at the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane

### The electrical conductivity analysis

The conductivity of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane sheet tested by electrochemical impedance spectroscopy (EIS) and the results are shown in the Cole-Cole plot in Figure 6. The resistivity obtained from Cole-Cole plots are used to calculate the conductivity of the polymer electrolyte membrane sheet. Conductivity the PVdF-LiBOB-ZrO<sub>2</sub> membrane sheet by the addition of ZrO<sub>2</sub> 0%, 2.5%, 5% and 7.5% are  $3.55 \times 10^{-8} \text{ Scm}^{-1}$ ;  $1.32 \times 10^{-7} \text{ Scm}^{-1}$ ;  $1.41 \times 10^{-7} \text{ Scm}^{-1}$  and  $1.65 \times 10^{-7} \text{ Scm}^{-1}$ , respectively at room temperature (Figure 7). The impedance test results show that the conductivity increases by the the addition of ZrO<sub>2</sub>. At a concentration of 0% ZrO<sub>2</sub>, LiBOB particles which serve as a conductor experienced agglomeration between the polymer matrixs, as shown in Figure 4.



**Figure 6.** Cole-Cole plot impedance test results of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane with a concentration of ZrO<sub>2</sub> (a) 0%; (B) 2.5%; (C) 5% and (d) 7.5%



**Figure 7.** Ionic conductivity of the PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane with a concentration of ZrO<sub>2</sub> (a) 0%; (B) 2.5%; (C) 5% and (d) 7.5%

The highest conductivity is at a concentration of 7.5% ZrO<sub>2</sub>. This is because ZrO<sub>2</sub> is a conductive metal. The increase in ionic conductivity are not significant to the increase of the addition of ZrO<sub>2</sub>, analysts SEM show that with the addition of ZrO<sub>2</sub> the pores is reduced, the particles become denser, so the ion moving space is limited and caused the ion electric conductivity is decreased[17]. The increase in electrical conductivity can be explained from the diffraction pattern (Figure 2). In the field of (1,1,1) at an angle  $2\theta = 31.480$  the phase is ZrO<sub>2</sub>. In 0% ZrO<sub>2</sub> the peak intensity is low. With increasing ZrO<sub>2</sub> from 2.5% the peak intensity increased and further increase in 7.5% of ZrO<sub>2</sub>.

From the Electrical conductivity test the addition of ZrO<sub>2</sub> increasing of the value of electrical conductivity. But the value of electrical conductivity is actually expected to go down (because the electrolyte materials is used as transfer media of ions from the anode to the cathode so that what is needed is the passage of ions), because the value is only changed



no more than rank one[18]. Then it can still be expected the electrical conductivity value will be increased with the addition of ZrO<sub>2</sub> which is needed in the next cell test.

## CONCLUSIONS

The PVdF-LiBOB-ZrO<sub>2</sub> polymer electrolyte membrane has been successfully prepared by methods doctor blade. The crystallinity index increases by the addition of ZrO<sub>2</sub>. The electrical conductivity obtained  $1.65 \times 10^{-7} \text{ Scm}^{-1}$  at room temperature on samples with the addition of 7.5% ZrO<sub>2</sub>. The addition of ZrO<sub>2</sub> results in increased ionic conductivity. The morphology of the sample surface looks flat, with the spread evenly additive and more denses with increasing ZrO<sub>2</sub> additives.

The addition of ZrO<sub>2</sub> to the PVdF-LiBOB polymer composite produces a better membrane, but does not provide a significant increase in electrical conductivity.

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