Li ION CONDUCTING POLYMER BASED ON POLYVINYLIDENE FLUORIDE AND Li TRIFLATE

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ABSTRACT

Li ION CONDUCTING POLYMER BASED ON POLYVINYLIDENE FLUORIDE AND Li TRIFLATE. A Series of polymer electrolyte based on Polyvinylidene Fluoride (PVDF) for solid state rechargeable lithium battery has been prepared by solution casting technique. Lithium triflate salt was used as filler with various compositions. Bulk nature and surface morphology of the polymer electrolytes were studied by X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM), respectively. The thermal properties of polymer and salt were confirmed by Differential Scanning Calorimeter (DSC). The electrical properties of electrolyte polymer membrane were studied by using impedance spectrometer. It was found that the highest ionic conductivity was obtained for PVDF + Li Triflate 10% (w/w) which is 4.5411×10^{-3} S/cm. It was also found that there was peak of each composition in the loss tangent suggests the presence of relaxing dipoles in the polymer electrolyte films. The peak shifts towards higher frequency side suggesting the speed up of the relaxation time.

Keywords : Polyvinylidene Fluoride, Lithium triflate, Ionic conductivity

ABSTRAK

POLIMER PENGHANTAR ION Li BERBASIS POLIVINILIDEN FLUORIDA DENGAN GARAM Li TRIFLAT. Serangkaian *polymer electrolite* berbasis *Polyvinylidene Fluoride* (*PVDF*) untuk digunakan pada baterai litium isi ulang telah dibuat dengan metode *casting*. Garam litium triflat dengan berbagai komposisi digunakan sebagai *filler* (sumber ion litium). Kristalinitas dan morfologi permukaan polimer elektrolit masing-masing diamati dengan *X-Ray Diffractometer* (*XRD*) dan *Scanning Electron Microscope* (*SEM*). Sifat termal polimer yang mengandung garam diukur dengan *Differential Scanning Calorimeter* (*DSC*). Sifat listrik polimer elektrolit dipelajari dengan menggunakan spektrometer impedansi. Didapatkan bahwa konduktivitas ionik tertinggi diperoleh pada penambahan Li Triflat 10% dengan nilai konduktivitas $4,5411 \times 10^{-3}$ S/cm. Juga didapatkan puncak *loss tangent* untuk tiap komposisi yang menunjukkan keberadaan relaksasi *dipole* di dalam *polymer electrolite*. Pergeseran puncak ke daerah frekwensi lebih tinggi menunjukkan waktu relaksasi semakin cepat.

Kata kunci : Poliviniliden Florida, Litium triflat, Konduktivitas ionik

INTRODUCTION

In our daily life at this time, we use a lot of electronic devices such as personal computers, cellular phone and digital camera. Increasing demands for such technologies sparked interest in the study of power sources, such as rechargeable lithium battery. The use of lithium metal offers the possibility of highly specific energy batteries.

A battery is composed of three components, anode (lithium metal), cathode (lithium metal oxide) and electrolyte. For the electrolyte, flammable liquid electrolyte is generally used. It leads to the problems such as a leakage and combustion due to production of gases upon overcharge or overdischarge process. Moreover battery performance is also related to the

lithium surface and to the lithium/electrolyte interface property [1,2].

The use of solid state electrolyte can solve these problems and so the search of an excellent solid electrolyte becomes very essential. Ion conduction is an important characteristic in development of solid electrolyte that covers the wide spectrum, ranging from inorganic crystalline, ceramics, glasses, polymer and composite materials. Solid-state ionics based on polymer have become interesting subject for more decades. The distinct advantages of polymer electrolytes over other solid electrolytes are unique electrical and mechanical properties, ease of fabrication into films of desirable size and thickness, and could be exceeds the performance of conventional liquid electrolyte systems. Electrolyte is the key component of the lithium polymer battery. There is a series requirement to choose the appropriate electrolyte, that include high ionic conductivity, good mechanical properties and compatibility with the electrode materials.

The first investigation on ionic conductivity of polymer electrolytes was reported by P.V. Wright in 1973. Extensive work has been carried out on solid polymer electrolyte based on Poly(ethylene oxide) (PEO) that include its modification by plasticization and by addition inorganic materials as the fillers to improve the mobility and conductivity of lithium ion [3-5]. PEO has demonstrated its good performance as a solid polymer electrolytes, however the high degree of crystallinity of PEO restrict its use in battery. Many efforts have been done to increase the conductivity of solid polymeric electrolyte including the use of many kinds of polymer as matrix and salt dissolved, use of blend polymer, gel electrolyte and hybrid electrolyte. Today commercial lithium polymer technology is based on gel type polymer membranes that exhibit semi solid properties. On polymer gel, the ions will move more freely than in the solid.

Research on polymer gels have been carried out, such as, the polymer poly (acrylo nitrile) (PAN), poly methyl methacrylate (PMMA), Poly-Capro ε Lactone (PCL), chitosan and PVDF [6-12]. PVDF is a polymer that is widely used in lithium battery and a many research has widely implemented to modify electrolyte material by using PVDF such as as blending with PMMA and PVAAc [13,14]. Although it has been widely applied in industry, but the mechanism of ion conduction in these polymers remain unsolved. PVDF has a high dielectric constant ($\varepsilon = 8.4$), which is effective to decompose the lithium salts to produce a lot of ions to be conducted in the electrolyte. C.Y. Chiang et al have conducted a study on the effect of salt $LiPF_6$ addition to the properties of gel polymer PVDF. They showed that the conductivity of PVDF increases linearly with higher added salt composition [15].

In this paper we will report the research on the PVDF polymer with $LiCF_3SO_3$ addition. Characterization was conducted on its electrical properties such as: conductivity, tan ∂ and impedance, microstructures and the changes in the thermal properties of PVDF $LiCF_3SO_3$ due to the addition of salt. The experiment result are compared with a previous study conducted by CY Chiang [15], which added different lithium salt ($LiPF_6$) to the polymer PVDF.

EXPERIMENTAL METHOD

Solid Polymer Electrolyte Preparation

The solid polymer electrolyte film is prepared by the solution cast technique. Main material to synthesize polymer electrolyte was Poly (vinylidene fluoride), purchased from Sigma Aldrich with average MW = 534.000, and $LiCF_3SO_3$, purchased from Alfa Aesar and used without further purification. PVDF polymer was dissolved in N-methyl-2-pyrrolidon (NMP) followed by the addition of various amounts of $LiCF_3SO_3$ salt (0 - 40 %w/w) and stirred continuously with magnetic stirrer for several hours at 50°C until the PVDF powder and $LiCF_3SO_3$ salt have completely dissolved. The homogenous solution were poured on different clean and dry petri-dishes and allowed to evaporate slowly at 55°C in vacuum until solvent free film were obtained. The films were kept in desiccators with silica gel desiccant for further drying.

Characterization

X-Ray diffraction measurements were performed at room temperature using a Shimadzu X-Ray Diffractometer (XRD-610) on the 2θ (Bragg angles) range 5-60° at scan rate of 3°/minute. Differential Scanning Calorimetric measurement were performed by means of a Perkin-Elmer (DSC 7 series) system at a heating and cooling rate of 10 °C/min to observe the change of melting temperature of PVDF with different salt content. The surface morphology of electrolyte films were observed using Scanning Electron Microscope (SEM) type JSM-6510LA from JEOL used a gold coated film sample. A series of conductivity measurements, dielectric properties and tangent loss on PVDF-$LiCF_3SO_3$ film with different salt content were conducted by using an impedance spectroscopy (Hioki LCR Hi-Tester, Model 3522). Measurements were carried out in frequency range 42 Hz - 5 MHz at room temperature. The conductivity values (σ) were calculated from the equation :

$$\sigma = (1/R)(t/A) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

where :

   t = The thickness
   A = The area of the sample
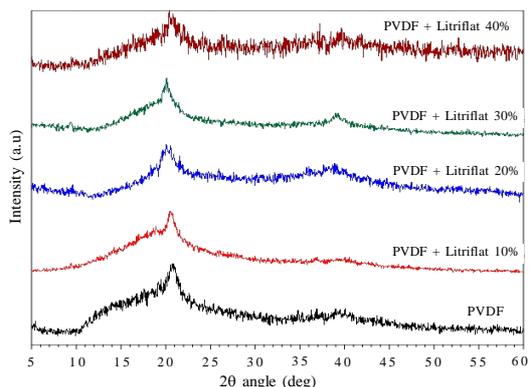
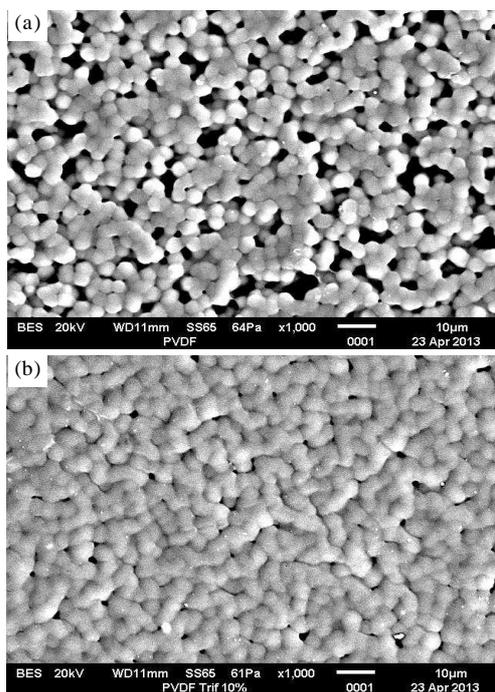***Figure 1.*** X-ray diffraction spectra of PVDF and PVDF + LiCF$_3$SO$_3$ (Li Triflate)

Figure 2. Scanning Electron Micrograph (x1000): (a). PVDF and (b). PVDF + LiCF$_3$SO$_3$ 10%

Those characterizations were performed at laboratory in Technology Center for Nuclear Industry Materials, BATAN, Indonesia

RESULTS AND DISCUSSION

XRD studies have been carried out in order to monitor the crystalline character of PVDF with the change of salt content.

Figure 1 shows the XRD pattern of PVDF film and PVDF + Li Triflate with different composition (10 % w/w to 40 % w/w). It is observed that PVDF (lowest graph) exhibits sharp reflection peak at angles $2\theta = 20.5°$ and broad peak at around $2\theta \sim 40°$ and illustrate various crystalline forms in PVDF. For PVDF film with 10% LiCF$_3$SO$_3$, it is observed that broad peak at $2\theta \sim 40°$, is disappeared, suggest a decrease in crystallinity and the degree of crystallinity of PVDF. Few differences are

observed between the pure PVDF with PVDF LiCF$_3$SO$_3$ salt blend film with composition 20-30% w/w. For PVDF films with composition LiCF$_3$SO$_3$ 40%, the peak intensity at an angle $2\theta = 20.5$ become broader and less prominent. This phenomenon is quite similar to the study of the PVDF films with LiPF$_6$ salt [15].

Although PVDF is not an ionomer, the CF bond in PVDF able to form a weak bond with the acid alkaline lithium ion, that can damage PVDF crystallinity.

Figure 2 is micrograph of PVDF film and LiCF$_3$SO$_3$ salt added one observed by Scanning Electron Microscope. It is shown that pure PVDF surface structures form a spherical grain with a size of about 5 µm and porously. PVDF is a polymer having a high dielectric constant, so that the surface tension is also high. Surface structure of the film is highly dependent on the drying process of the film from the solution in gel phase. The addition of salt LiCF$_3$SO$_3$ cause acid-base interactions between the salt and the polymer, thus affect on the crystallinity and surface tension. As shown in Figure 2(b) with the addition of salt, the spheres become larger with a smooth surface and the pore size is also become smaller. The addition of salt causes the polymer swelling and form amorphous structure.

Figure 3 shows the curves of the thermal properties measured by Differential Scanning Calorimeter (DSC). DSC curves show the endothermic melting point for all samples. The melting point of pure PVDF is 161.54 °C, with the addition of LiCF$_3$SO$_3$ salt there is decreasing in the melting temperature. The addition of salt has changed the structure of PVDF polymer crystals become amorphous. The lowest melting point 156.58° is found in the sample with 10% salt content and it is an irregularity, because in the previous study with different salt the melting point decrease with addition of more salt. These results are consistent with the trend of X-ray diffraction pattern shown in Figure 1 and the conductivity values aforementioned below .

Type of salt added gives a different effect on the nature of the polymer PVDF. Studies on the effects of adding salt LiPF$_6$ in PVDF polymer produces an order, whereby the greater the concentration of salt added the structure more amorphous, so that the lower melting
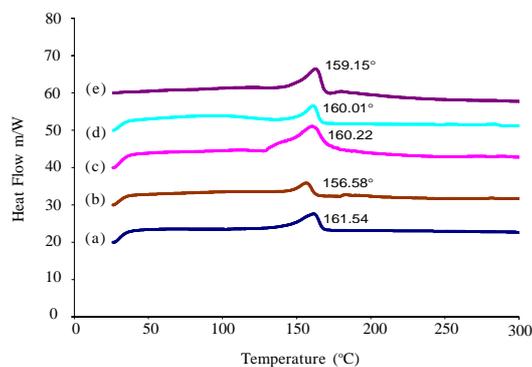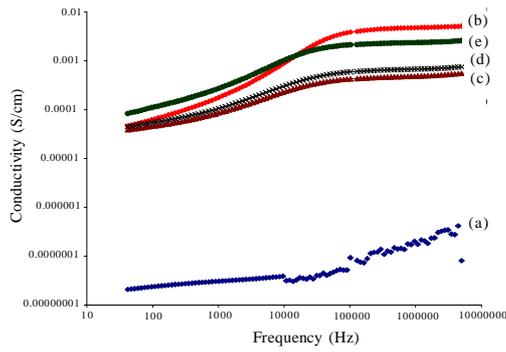

***Figure 3.*** DSC Curve of (a). 0%, (b). 10%, (c). 20%, (d). 30% and (e). 40% LiCF$_3$SO$_3$ in PVDF

Figure 4. Variation of a.c conductivity with frequency of PVDF and $LiCF_3SO_3$ (a). 0%, (b). 10%, (c). 20%, (d). 30% and (e).40%

Table 1. Parameter obtained from experimental data fitting of PVDF and x% $LiCF_3SO_3$

$LiCF_3SO_3$ conc.	σ_0 (S/cm)	A	n
0%	2.3725×10^{-8}	6.057×10^{-10}	0.34124
10%	4.5411×10^{-3}	2.3066×10^{-7}	0.51204
20%	4.6075×10^{-4}	3.5925×10^{-10}	0.81770
30%	6.5006×10^{-4}	2.1643×10^{-10}	0.85627
40%	2.3057×10^{-3}	1.2826×10^{-10}	0.95788

temperature of sample while increasing the ionic conductivity. This phenomenon was not observed in the addition of salt $LiCF_3SO_3$. This is likely due to differences in the stereochemistry of salt $LiPF_6$ and $LiCF_3SO_3$ so that it gives effect on the Lithium ion dissociation in the polymer matrix. Beside that the solubility of lithium salts in nonaqueous solution also are affected by the anion size of lithium salt, where the bigger anions the solubility of lithium salts would increase ($CF_3SO_3^- > PF_6^-$) [16].

Figure 4 shows the change of ac conductivity as a function of frequency for PVDF films that have added by $LiCF_3SO_3$ salt at various concentrations and were measured at room temperature. The ac conductivity patterns show a frequency independent plateau in the high frequency region. This behavior obeys the universal power law, $\sigma_{(\omega)} = \sigma_0 + A\omega^n$, where σ_0 is the dc conductivity (frequency independent plateau), A is the pre-exponential factor and n is the fractional exponent and its value is between 0 and 1 [17]. The value of σ_0, A and n were obtained by fitting $\sigma_{(\omega)}$ to the $\sigma_{(\omega)} = \sigma_0 + A\omega^n$ and tabulated in Table 1. For ionic conductor materials, the value of n ranges between 1 and 0.5, which shows the ideal pathway of ion trip in polymer matrix (for n = 1) and the length of the winding pathway for n = 0.5. In Figure 4 curve a is conductivity of pure PVDF and has the lowest conductivity because this polymer is isolator and there is no ion to be conducted. Curve b, c, d and e are curves of PVDF that containing $LiCF_3SO_3$ 10%, 20%, 30% and 40% respectively. Conductivity of polymer systems are increased as frequency function is higher, and achieved frequency independent plateau at region up to 10.000 Hz for all PVDF containing $LiCF_3SO_3$.
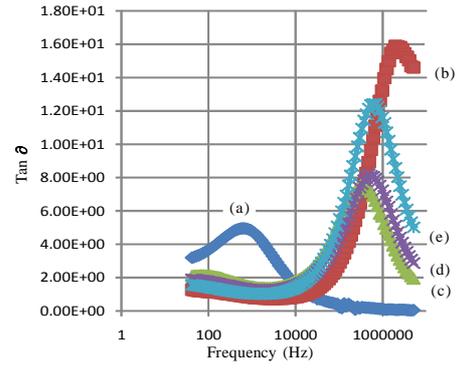
Figure 5. Variation of tan ∂ of PVDF film with frequency for different concentration of $LiCF_3SO_3$ (a). 0%, (b). 10%, (c). 20%, (d). 30% and (e).40%

From the Table 1, it can be seen that dc conductivity (σ_0) increases with increasing salt content. The higher ionic conductivity is related to more ions in polymer matrix. Fractional exponent (n) value also increase with increasing salt content. The deviation is found for PVDF film with 10% salt content, which the value of σ_0 is the highest but its fractional exponent is the lowest, it is means that lower salt content cause the ion is free to move but with the tortuous pathway.

Figure 5 shows the variation in loss tangent as a function of frequency for the PVDF films for various compositions of $LiCF_3SO_3$ salt and measured at room temperature. There is peak appears at high frequency about 1 MHz for all samples PVDF added $LiCF_3SO_3$ salt, but for PVDF film the peak appears at a lower frequency. This suggests the existence of dipole dipole relaxation in all samples. Peak intensity indicates the easiness of ion movement within polymer matrix which ions in the sample containing 10% $LiCF_3SO_3$ move most freely and the sequence of ion movement of PVDF/$LiCF_3SO_3$ as following : 10% > 40% > 30% > 20% > 0%. This sequence is associated with changes in the crystal structure due to the addition of salt $LiCF_3SO_3$ to PVDF. For the amorphous samples, the ions will move easier in the polymer matrix. Referred to the XRD profile in Figure 1 shows that for the sample with 20% and 30% salt composition, the angle position (2 θ) = 20.5 ° and 40 ° showed increased crystallinity in the two samples, hindering the ions movement that lead in reducing the
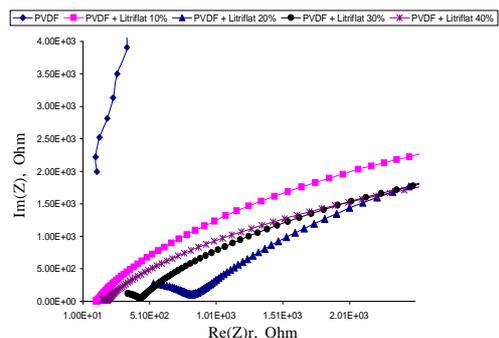
Figure 6. The impedance spectra of PVDF + x% m/m $LiCF_3SO_3$

value of conductivity compared to 10% $LiCF_3SO_3$ composition.

Increase of crystallinity and the formation of crystalline domains are probably due to a domain PVDF dissolved in $LiCF_3SO_3$. Further addition of salt (40%) increases the conductivity as a result of crytallinity decrease (see Figure 1, XRD profile) and increased of molecules movement (tan ∂). This occurs because the domain size of PVDF soluble in $LiCF_3SO_3$ getting smaller or in other words miscibility occurs between PDVF and $LiCF_3SO_3$. Tangent delta for PVDF appear at low frequency indicates inflexibility of PVDF molecules

To further study the conductivity properties of PVDF/$LiCF_3SO_3$ polymer electrolytes, their resistivity component was measured by impedance spectroscopy. The impedance spectrum shown in Figure 6 measured under potential 1 volt. It can be seen that PVDF has very low conductivity, did not show capacitance properties, only resistivity. At the high frequency region shown that all the salt added PVDF film forming semicircle pattern where migration of the ionic salt $LiCF_3SO_3$ occurs along passive layer, the polymer PVDF. The resistance of intermediate frequency, as shown on Figure 5, represented the PVDF $LiCF_3SO_3$ capacitance charging process. The order of capacitance values of PVDF/$LiCF_3SO_3$ are as follows : 10%>40%>30%>20%.

CONCLUSION

It have been studied the properties of solid polymer electrolyte PVDF and $LiCF_3SO_3$ salt with different compositions. XRD data show that salt addition has changes the crystallinity of PVDF, because interaction between ion Li^+ and fluorine in polymer is effective to disorder the crystallinity of PVDF. The microstructure data showing different morphology, which film added salt has smooth surface. Addition of $LiCF_3SO_3$ can reduce the melting temperature of PVDF. Salt addition also increase the dc conductivity until 4.5411×10^{-3} S/cm and highest conductivity was obtained for PVDF + $LiCF_3SO_3$ 10% . So that PVDF + 10% $LiCF_3SO_3$ composition could be a good candidate for solid polymer electrolyte materials of rechargeable lithium battery.

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