



Preparation and Characterization of Fly Ash/PVdF-PAN Composite Polymer Electrolyte Membranes and their Potential Use for Li-ion Batteries

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Abstract : This paper presents an effort to increase mechanical and conductivity properties of PVdF-PAN electrolyte membrane via addition of fly ash. The polymer electrolyte membranes were prepared by non-solvent induced phase separation (NIPS) method using different concentration and particle size of fly ash. The prepared membranes were then characterized including surface morphology (by SEM), surface chemistry (by FTIR spectroscopy), porosity, electrolyte uptake, crystallinity (by X-Ray Diffraction), mechanical properties and ionic conductivity. The results show that the addition of fly ash decreases membrane crystallinity and increases membrane porosity. Further, increasing both tensile strength and ionic conductivity about two times greater than the membrane without addition of fly ash is clearly observed. In general, the results suggest that the electrolyte membranes prepared with addition of fly ash show better characteristics with respect to Li-ion batteries application.

Keywords : Fly ash, Li-ion batteries, PVdF- PAN polymer electrolyte membrane, composite embrane.

1. Introduction

In the last decade, remarkable development of transportation and portable devices has led to strong necessity of safe and high energy storages[1]. Lithium-ion batteries represent one of the major successes of modern electrochemistry[2]. Compared with other conventional battery systems (e.g., the lead-acid, nickel-cadmium and nickel-metal hydride batteries) lithium-ion batteries have main advantages, which are rechargeable power sources, stable for over 700 cycles, compact and lightweight. All these advantages can reduce both costs and the environmental impacts. Furthermore, due to high energy and power densities, they are recognized as the greatest battery performance among other conventional battery systems [3]. In recent years, lithium-ion batteries have been used in electric vehicles (EVs), hybrid-electric vehicles (HEVs), and as a power source for a wide variety of portable electronic equipment such as cellular phones, digital cameras, and laptops [4].

A battery is an electrochemical power source composed of several unit cells[2]. Each cell consists of three major components, which are a positive electrode, a negative electrode and an electrolyte separating them. Liquid electrolyte is deployed between two electrodes as a connector for ion transfer and it restricts direct contact between them. Replacement of the liquid electrolyte by a solid electrolyte has been proposed. The main advantage of this approach is that it avoids leakage of electrolyte solution, which is one of the most undesirable features of many batteries due to potentially explosive [1]. Thus, polymer electrolyte is an ideal successor for liquid electrolyte in Li-ion batteries system.

Poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC), poly(propylene oxide) (PPO), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVdF) have been considered as benchmark polymers for the preparation of polymer electrolytes [5-7]. Among those benchmark polymers, PVdF has received considerable attention due to its good electrochemical stability and affinity to electrolyte solutions, exhibits high ionic conductivities (in the range of 0.1-1.0 mS cm⁻¹) [8] and high dielectric constant ($\epsilon \approx 8.4$) [2]. These features are useful in dissociating lithium salt to lithium ions. The problem restricting the use of PVdF-based polymer electrolytes is their crystalline structure that hinders the migration of Li⁺ and hence batteries with PVdF-based electrolytes have lower charge/discharge capacities. Besides PVdF, PAN has also received significant attention for a polymer electrolyte material. PAN-based electrolytes have shown interesting characteristics, i.e. higher ionic conductivity than PVdF membranes, good thermal and mechanical stabilities, good structure for electrolyte uptake and compatibility with the lithium electrode [9,10]. Besides these characteristics, PAN can minimize the formation of dendrite growth during the charging/discharging process of Li-ion batteries [10]. However, the limitation for using PAN-based membrane is the possibility of liquid extraction from the gel for long term storage [9]. Blend of PVdF and PAN may produce polymer electrolytes with both features. Previous reported literature of blending PVdF-PAN polymer electrolyte showed better porosity and elongation than pure PVdF or PAN. However, they showed inferior mechanical strength [11] and relatively low ionic conductivity. Hence, augmenting of material to increase mechanical and ionic conductivity of polymer electrolytes is very interesting. Thus, in this study PVdF and PAN are used as the polymer materials.

One of the most promising ways to improve the electrochemical and mechanical properties of polymer electrolytes is by the addition of ceramic fillers [6,12,13]. In this regard, fly ash (FA) could be a good candidate as an additive for PVdF and PAN composite membranes. It was reported that FA has good thermal and mechanic properties, good permeability and porosity to adsorb electrolyte solution [14]. Moreover, compared with common commercialized ceramic membrane materials such as alumina, zirconia, titania and silica, which have expensive cost, fly ash is free or extremely cheap [15]. Abundance of fly ash in Indonesia, which is known as solid waste of coal combustion, is another benefit. Indonesian coal contains typically 2-15% ash with 80-90% of ash will be resulted as fly ash. In this work, PVdF-PAN polymer electrolyte membranes are prepared using phase inversion method with addition of fly ash as composite filler. More specifically, the impact of fly ash addition on the characteristics of PVdF-PAN polymer electrolyte membrane for Li-ion batteries is investigated.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVdF; Mw ~534000) and polyacrylonitrile (PAN; Mw 150000) as primary materials were purchased from Sigma-Aldrich. *N,N'*-dimethylformamide (DMF), lithium perchlorate (LiClO₄; battery grade, dry, $\geq 90.5\%$), propylene carbonate (PC; anhydrous, 99.7% and the water content is $<0.002\%$) were purchased from Sigma-Aldrich. Acetone and *n*-butanol were purchased from Merck. Fly ash (FA) as filler was obtained from steam power plant in Jepara, Central Java, Indonesia.

2.2. Preparation of polymer membranes and polymer electrolyte membranes

The polymer membranes were prepared by using phase inversion method. The membrane preparation followed the work of Li et al. [16] and Susanto and Ulbricht [17] with some modifications. Initially, the experiments were performed by preparing various concentration (0, 5, 10, 15% wt. of fly ash) of homogeneous fly ash dispersion in DMF/Acetone solvent mixture (with DMF/Acetone ratio was 7/3). Then, the experiments were continued by dissolving 10% wt. of PVdF and PAN polymers (with ratio PVdF/PAN was fixed to be 75/25) into fly ash-solvent dispersion. The polymers were dissolved at temperature of 70°C with stirring for 8 hours to obtain a homogenous polymer-fly ash solution. Thereafter, the polymer solution was cast with a thickness of 200 μ m using a steel casting knife on a glass substrate. It is important to mention that the casting was performed in an air atmosphere with relative humidity within the range of 60-70% and temperature of 25 \pm 3 °C. The "proto-membranes" were then coagulated into a water bath with temperature of $\sim 26^\circ\text{C}$ over 24 hours. In order to remove the remaining solvent and other components, the resultant membranes were washed by soaking in water for at least 2 hours before drying. After being dried in room temperature over 18 hours

followed by drying in oven at 40°C for about 6 hours, polymer membranes were obtained. Viscosity of polymer-fly ash solution was measured by using viscometer DV-I Brookfield.

In order to minimize the effect of particle size, the fly ash size used in this experiment was determined to be 150 and 300 meshes, which correspond to 74 – 105 µm and 37 – 53 µm in diameter, respectively. Polymer electrolyte membranes were prepared by soaking polymer membranes in a 1 M solution of LiClO₄ in a PC (volume ratio 1:1) at room temperature for 24 hours.

2.3. Fly ash and membrane characterizations

The composition of fly ash was characterized by using atomic absorption spectroscopy (AAS), whereas sieve shaker was used to determine the size of fly ash particles. Membrane characterizations included porosity, uptake of electrolyte solution, morphology, chemical structure and crystallinity. In addition, mechanical and electrochemical properties were also investigated.

Porosity of polymer membranes was determined using *n*-butanol uptake. For this purpose, polymer membranes were immersed in *n*-butanol for 2 hours. The porosity of the membrane was calculated by using the following equation:

$$\% \text{ porosity} = \frac{m_a - m_o}{\rho \times V} \times 100 \quad (1)$$

where *m_a* and *m_o* are the mass of membranes after and before immersion in *n*-butanol, respectively; ρ is the density of *n*-butanol and *V* is the bulk volume of membrane.

The percentage of electrolyte uptake by membranes was determined by using the following equation:

$$\% \text{ electrolyte uptake} = \frac{M_a - M_b}{M_b} \times 100 \quad (2)$$

where *M_a* and *M_b* are the mass of membranes after and before immersion in the liquid electrolyte, respectively.

By calculating the value of retention ratio of polymer membranes, leakage of electrolyte solution then can be determined [18]. Retention ratio (*R*) was described as a ratio of the amount of electrolyte in membrane after 2 hours test to the amount of electrolyte in membrane before testing. The retention ratio (*R*) was calculated by using the following equation:

$$R = \frac{M_i}{M_s} \quad (3)$$

where *R* is the relative absorption ratio of the liquid electrolyte, *M_s* is the mass of the polymer electrolyte when the membrane is fully saturated with the liquid electrolyte, and *M_i* is the mass of the polymer electrolyte after a time interval when the saturated polymer electrolyte is squeezed by pressing it between two filter papers. Finally, leakage was calculated by the following equation:

$$\% \text{ Leakage} = (1 - R) \times 100 \quad (4)$$

Scanning electron microscopy (SEM) of FEI type inspek-550 was used to visualize morphology of the membrane surface. The chemical structure of membranes was analyzed using Fourier transform infrared spectrophotometer (FTIR) Shimadzu IR Prestige-21. The crystallinity of polymer membranes was detected by using X-Ray Diffraction (XRD) PANalytical X'pert Pro. Texture Analyzer (ASTM 1983, FG/SPAG 01/2650) was applied to determine the mechanical properties of membranes, such as tensile strength, extension at maximum, and modulus young. The bulk resistance measurement using milliohm meter was performed to calculate ion conductivity of polymer membranes as indicator of electrochemical property of membranes. The conductivity was determined using the following equation:

$$\text{Conductivity } (\delta) = \frac{d}{RbA} \quad (5)$$

where R_b is the resistance (ohm), d and A are the thickness and area of the membranes tested, respectively.

3. Results and Discussion

3.1. Characteristics of fly ash

The AAS analysis showed that the fly ash used in this study contains 36.17% of SiO_2 and 28.60 % of alumina. According to Ahmaruzzaman [14] the fly ash used in this study should be in the group of F type due to the content of silica and alumina up to 50%. Further, this result suggests that this fly ash is suitable as ceramic filler for polymer electrolyte application due to its high adsorption capacity.

3.2. Membrane structures

3.2.1. Morphology

It is expected that the membranes for Li-ion battery application should have high porosity and fine pore distribution. In addition, filler distribution in the membrane polymer has significant influence on membrane performance [19]. Fig.1 shows SEM images from visualization of membrane surface for different preparation conditions. The presence of fly ash in the membrane can clearly be observed. In general, the membrane pores are distributed within the range of 0.05 – 2 μm depending on the fly ash content and fly ash particle size. For the same fly ash size (Fig. 1 (a), (b) and (d)) the increase in fly ash content increases the membrane pore density with the pore size tends to decrease. However, at fly ash concentration of 15% the increase in membrane pore size with fly ash grain inside the pore can be clearly seen (Fig. 1 (d)). Uniform distribution of fly ash in polymer matrix seems to have influence on the formation of membrane with narrow pore size distribution. At high fly ash concentration the grains get too close to each other leading to greater pore size formation.

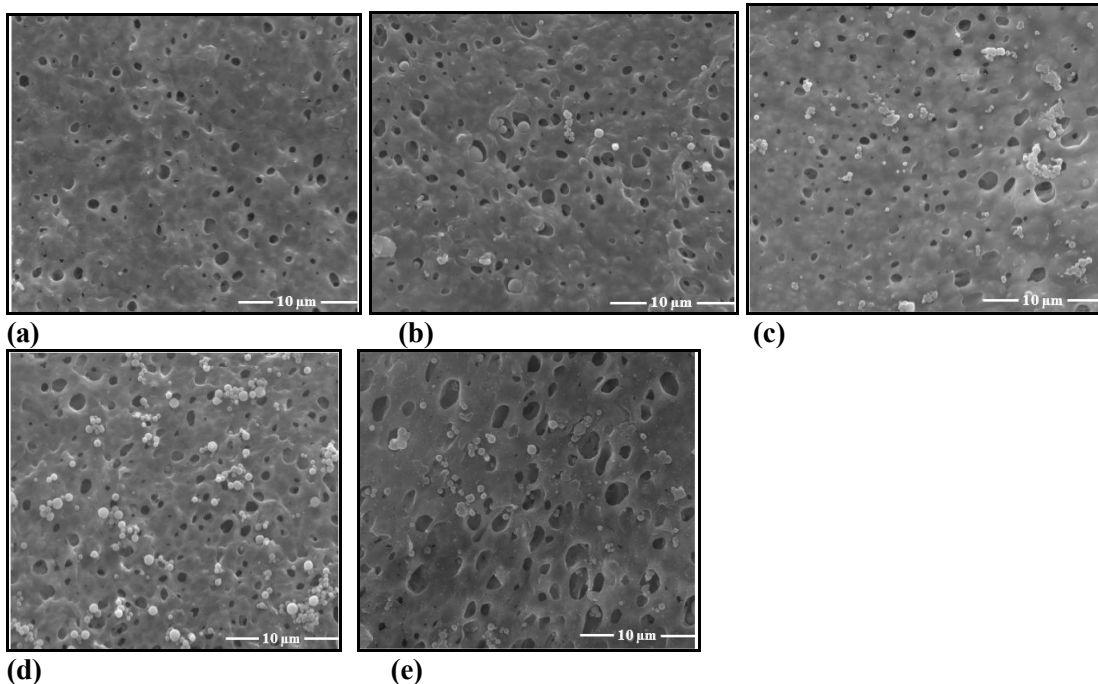


Fig. 1. SEM images of the membranes (10.000 x): (a) 0 % fly ash, (b) 5% fly ash 300 mesh, (c) 10% fly ash 150 mesh, (d) 10% fly ash 300 mesh, (e) 15% fly ash 300 mesh.

For similar fly ash content (10%), the membranes prepared with smaller fly ash particles (cf. (c) and (d)) generate more pores (higher pore density). The reason for this observation is that the smaller fly ash size the higher possibility of fly ash to be dispersed homogeneously in the polymer matrix. It is also observed that the resulting pores were more uniform for smaller size of fly ash particle added.

3.2.1. Chemical structure

Functional group structure of polymer membrane was observed by Fourier transform infrared (FTIR). Fig. 2 shows the IR spectra of PVdF-PAN membranes with the addition of 10% fly ash 300 meshes. Typical spectra of PVdF membrane can be observed by peaks at 1404 cm^{-1} and 1180 cm^{-1} representing deformation and stretching of $-\text{CF}_2$, respectively. Then, the peak at 1070 cm^{-1} shows the characteristic of $-\text{CN}$ of PAN. These results are in agreement with previous results by Liu *et al.* [20] and by Belfer *et al.* [21]. This IR spectrum indicates that blending process did not change the chemical structure of PVdF. In addition to the presence of PAN, the peak at $\sim 1070 \text{ cm}^{-1}$ could also indicate the stretching of Si-O-Si as reported by Kakiuchi *et al.* [22]. The band at 440 cm^{-1} which can be attributed to Si-O-Si rocking vibration of silica is also observed. Further, influence of fly ash filler can be detected at 761 cm^{-1} representing C-OH as a result from the formation of a weak acid-base complex between -OH group of filler particles and $-\text{C}$ of polymer chain.

3.2.2. Crystallinity

The crystalline part of PVdF hinders the migration of Li^+ resulting PVdF-based electrolyte batteries have lower charge/discharge capacities [23]. In this work, the effect of fly ash addition on PVdF-PAN membrane crystallinity is investigated. The result is presented in Fig. 3.

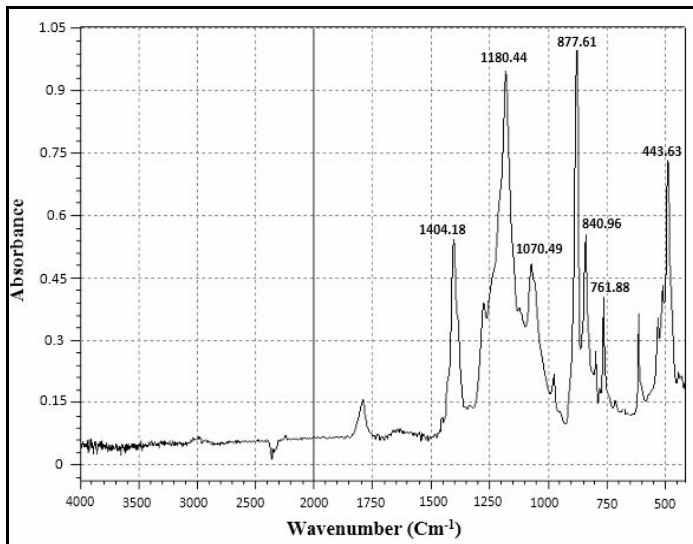
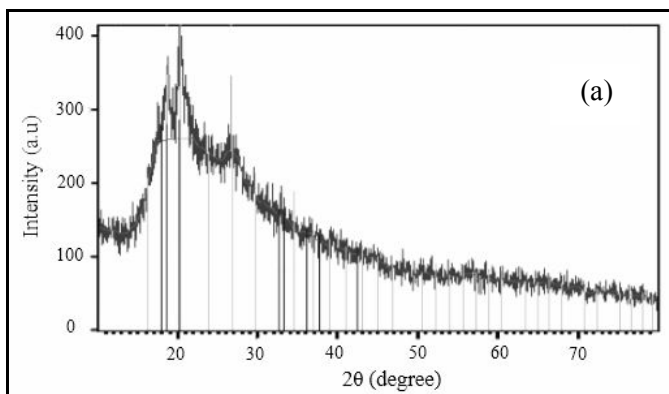


Fig. 2. IR spectra of PVdF-PAN membrane added by 10% fly ash 300 mesh.



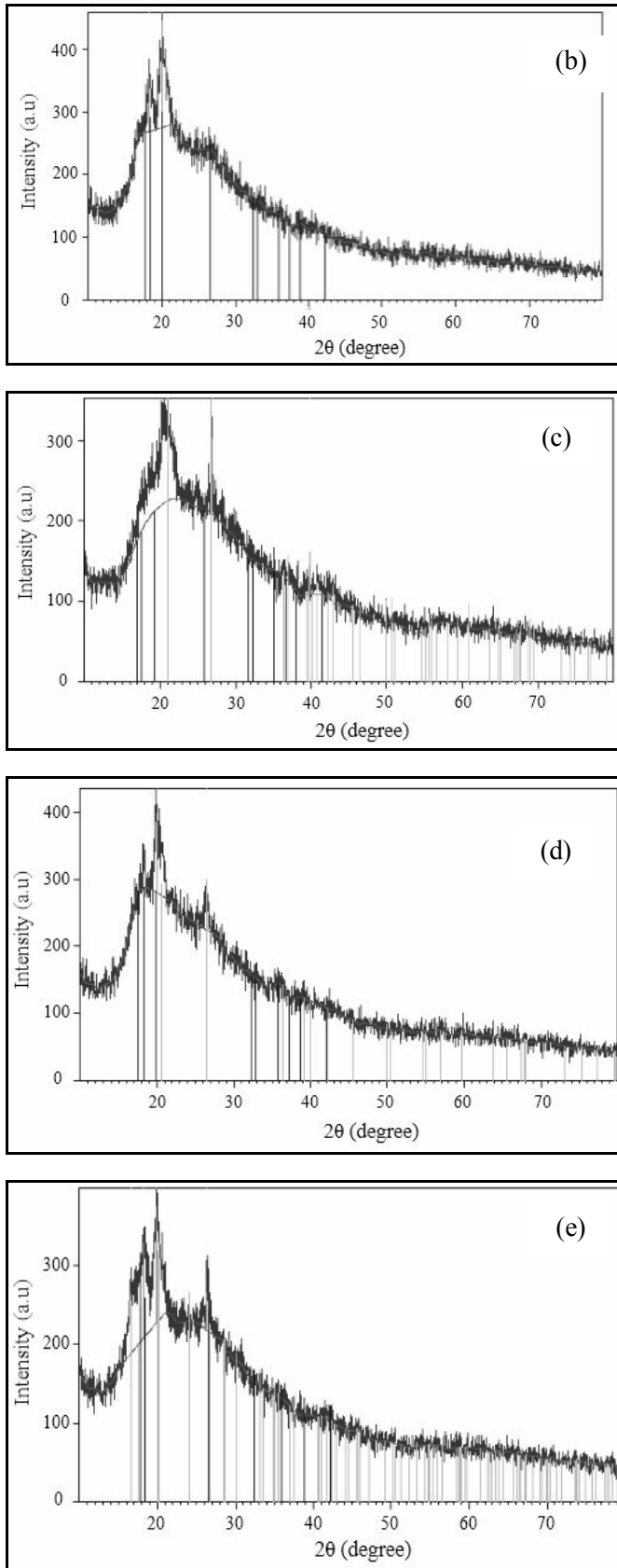


Fig. 3. XRD spectra of polymer membranes : (a) 0 % fly ash, (b) 5% fly ash 300 mesh, (c) 10% fly ash 150 mesh, (d) 10% fly ash 300 mesh, (e) 15% fly ash 300 mesh.

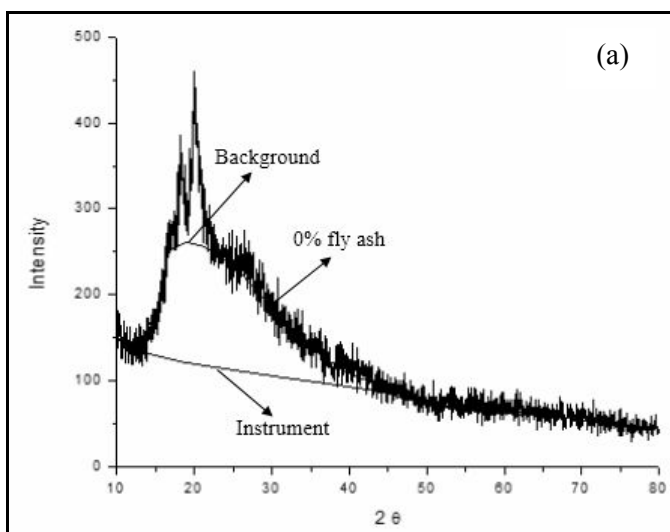
Fig. 3 exhibits X-Ray Diffraction (XRD) spectra of the polymer membranes. The crystalline structure of PVdF membranes is characterized by weak peak at $2\theta = 18.3$, the sharp peak at $2\theta = 20$ and the broad peak at $2\theta = 25$. This observation is in agreement with previous results reported by other research groups (e.g., [24,25]). The XRD spectra of each membrane were then analyzed and integrated to obtain crystallinity of membranes. Fig. 4(a) shows XRD analyzing graphic of the PVDF-PAN membrane with 0% fly ash, while Fig. 4(b) displays an integration graphic result.

Crystalline phase of membrane is represented by large area between sample and background line, whereas large area between background and instrument line represents amorphous phase. In Fig. 3, each phase depicts large area of peaks and broadening of diffraction peaks, respectively. Crystallinity of membranes can be calculated by dividing large area of crystalline phase to total area of crystalline and amorphous phase. As also suggested in previous studies [24,25], the broadening and lowering intensity of diffraction peaks after incorporating nano-sized fly ash fillers observed in this result suggest the decrease in crystallinity of PVd F-PAN. Further, Table 1 shows the percent of crystallinity resulted from the calculation by analyzing and integrating XRD spectrums as already described (Fig. 4).

Table 1. Crystallinity of various polymer membrane samples

Samples	Large area of phase		% Crystallinity
	Amorph	Crystalline	
0% Fly ash 300 mesh	1615	761	32.0
5% Fly ash 300 mesh	2026	710	26.0
10% Fly ash 150 mesh	2146	664	23.6
10% Fly ash 300 mesh	2329	586	20.1
15% Fly ash 300 mesh	1974	809	26.4

The reason for the decrease in crystallinity has been well explained in previous publications [25,26]. It can be attributed to the formation of a weak acid-base complex between the polar bond of PVdF-PAN (C-F and C-N) and the nano-sized fly ash filler, which retards the ordering of crystalline regions in PVdF-PAN. The regular structure of polymer chains may be obstructed by the cross-linking centers formed by the Lewis acid group of ceramic filler (e.g., -OH group of alumina surface in fly ash) with polar group of the polymer (-F and -N atom polymer chain) [25,26]. Thus, degree of crystallinity of the membranes is decreased with the addition of ceramic nanoparticles. In this work, the optimum condition is obtained at the membrane with 10% fly ash and 300 meshes.



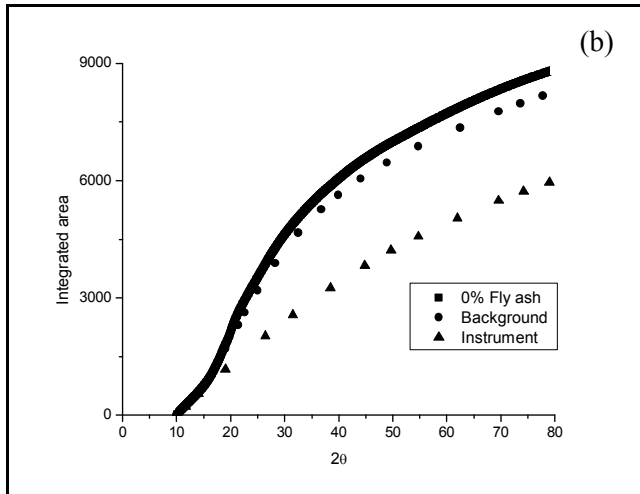


Fig. 4. (a) XRD analyzing graphic of 0% fly ash membrane, (b) XRD integration graphic result of 0% fly ash membrane.

For the same concentration of fly ash filler, membranes with smaller size of fly ash (300 meshes or equal to 37-53 μm) have a better role in decreasing crystallinity than 150 meshes due to their larger surface area. Increasing surface area creates more bonds between polymer chains and filler particles, which will reduce the crystalline structure. In addition, previous report explained that crystallinity may be reduced by the inhibition of crystallization by ceramic fillers during the solidification process, which reduces the volume fraction of crystalline phase in the polymer [27]. As a consequence from the decrease in crystallinity, melting point of membranes will be improved. This observation suggests that membranes with addition of fly ash fillers are suitable for Li-ion application as they have great resistance to temperature changing.

3.3. Characteristics of polymer membranes

3.3.1. Porosity

Porosity of polymer membrane is recognized as a ratio of pore volume to total volume of membrane. The membranes with higher degree of porosity show an overall large increase in the pore surface area resulting higher uptake of the electrolyte solution. The results of porosity measurement determined by *n*-butanol uptake are presented in Table 2. First of all, it is seen that the viscosity of polymer solution increases with increasing FA content. Secondly, the membrane porosity would first rise steeply reaching a maximum value with increasing FA content. However, further increase in FA decreases the membrane porosity. The optimum value is obtained at FA content of 10% with 300 meshes. This observation can be explained via competition between the increase in both surface area and viscosity of polymer solution caused by increasing FA content. The increase in surface area due to addition of fly ash particle would increase membrane porosity. In contrast, the increase in viscosity as the fly ash content in polymer solution was increased would decrease the porosity due to decreasing rate of phase separation process during solidification.

Table 2. Characteristics of various polymer membranes

Fly ash concentration (% wt.)	Size of fly ash (mesh)	Porosity (%)	Viscosity (cP)	Uptake solution (%)	Leakage (%)
0	-	66.5	344	322.7	20.6
5	150	67.8	452	355.3	16.8
5	300	69.1	460	360.2	15.2
10	150	69.4	502	394.7	14.7
10	300	75.5	508	409.3	6.9
15	150	71.7	518	368.7	17.9
15	300	69.7	532	370.4	18.4

3.3.2. Uptake solution

Uptake solution is an indicator describing the ability of the polymer membrane to absorb the electrolyte solution. Higher uptake means that more Li⁺ ions exist in the same volume of polymer electrolyte [28]. The measurement results of uptake solution of membranes are presented in Table 2. Interestingly, it is shown that there is a significant influence of fly ash addition on the electrolyte uptake solution, i.e. all membranes with fly ash fillers exhibit higher uptake solution. Pristine PVdF-PAN membrane shows an uptake solution of 323%, whereas membranes with fly ash have uptake solution ranging from 355% to 409%. The highest uptake solution is shown by the membrane with 10% fly ash 300 meshes. Apparently, this result is related with porosity, surface area and crystallinity of the membrane.

As explain before, the membranes with higher porosity result in higher uptake of the electrolyte solution. Fig. 5 shows the correlation between crystallinity and electrolyte uptake solution of membranes. The lower crystallinity the higher electrolyte solution uptake is observed. Amorphous structure should have higher electrolyte uptake solution. The amorphous flexible polymer matrix is favorable in increasing space for electrolyte solution. Consequently, membranes with lower crystallinity have favorable feature in absorbing electrolyte solution [3].

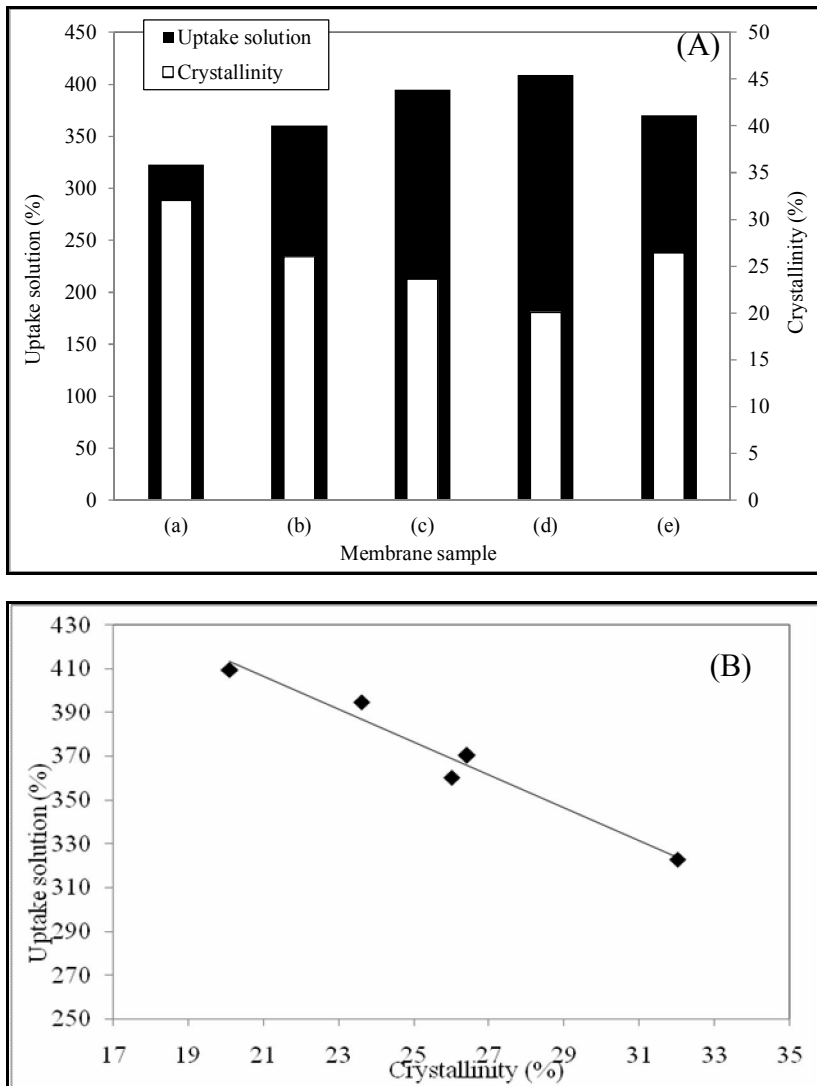


Fig. 5.(A) Crystallinity and uptake solution of various polymer membrane samples:(a) 0 % fly ash, (b) 5% fly ash 300 mesh, (c) 10% fly ash 150 mesh, (d) 10% fly ash 300 mesh, (e) 15% fly ash 300 mesh.(B) Correlation between crytallinity and electrolyte uptake solution.

3.3.3. Leakage

The leakage of electrolyte solution is very important for predicting the cycling performance of lithium ion batteries. To investigate the leakage of electrolyte, a situation was simulated as same as working batteries by placing the polymer membrane between two filter papers. By calculating the value of retention ratio, leakage can be determined (using Eq. (4)). The results are presented in Fig. 6.

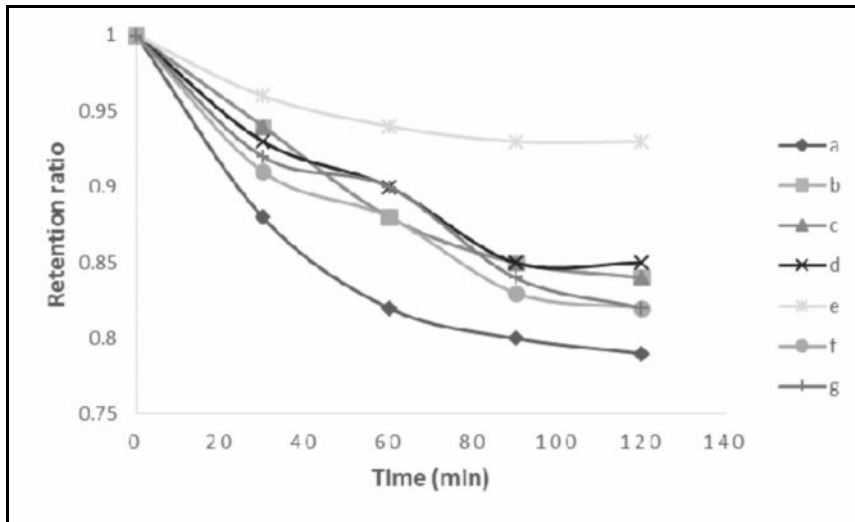


Fig. 6. Graphic of retention ratio during 120 minutes testing: (a) 0 % fly ash, (b) 5% fly ash 150 mesh, (c) 5% fly ash 300 mesh, (d)10% fly ash 150 mesh, (e) 10% fly ash 300 mesh, (f) 15% fly ash 300 mesh, (g) 15% fly ash 300 mesh.

As shown in Fig. 6, the highest retention ratio (i.e. 93.1%) is observed for the membrane sample (e), which was prepared with 10% fly ash and 300 meshes. The lowest retention ratio (i.e. 79.1%) is demonstrated by the membrane (a), which is PVdF-PAN polymer membrane without addition of fly ash. As discussed before, sample with 10% fly ash with 300 meshes has high porosity, relative uniform pore size and low crystallinity. The leakage of the electrolyte solution decreases with decreasing membrane pore size resulting in higher resistance for electrolyte to leave from membrane. In addition, the amorphous swollen phase also influences partially to tight hold of electrolyte solution and prevents the solution's leakage. Consequently, leakage of electrolyte solution can significantly be reduced, i.e. from 20.6% for pristine PVdF-PAN membrane to 6.9% for optimum condition.

3.4. Mechanical properties

Good mechanical strength is strongly needed because a battery must be safe and stable. Mechanical test results of membranes, which include tensile strength, maximum extension and modulus Young, are presented in Table 3.

Table 3. Mechanical properties of the various membranes

Fly ash concentration (% wt.)	Size of fly ash (mesh)	Porosity (%)	Viscosity (cP)	Uptake solution (%)
0	-	8.11	23.52	3.36
5	150	11.25	22.83	11.6
5	300	11.87	26.03	2.88
10	150	13.2	17.17	6.02
10	300	14.59	21.02	2.54
15	150	14.8	12.15	16.28
15	300	16.36	14.30	12.88

Table 3 shows that the presence of fly ash particles improves the tensile strength of membranes. The possible reason for this observation has been well explained by Wu et al. [29]. They stated that the small size and large surface area of filler particle results in a large contact area with the polymeric matrix. When material is stuck, more micro-cracking will absorb more impact energy. Therefore, further expansion of the cracks is blocked. Further observation showed that the tensile strength of membranes incorporated with fly ash filler is higher than the pristine PVdF-PAN membrane. Both the increase in fly ash concentration and the decrease in particle size of fly ash increase membrane tensile strength. The highest tensile strength is obtained by the membrane prepared with 15% fly ash with 300 meshes.

Maximum extension often reflects the impact performance of material and the impact resistance shown by the material toughness. The higher toughness the smaller risk of the membrane collapses. Maximum extension is observed to decrease in the presence of the ceramic particles adversely affects the flexibility of the polymer. This result is in agreement with previous result reported by Raghavan et al. [18]. Young modulus measurements, which represent stiffness of membranes, show opposite trend with extension at maximum. As modulus young decreases, more load can be accepted by the membrane. The load-bearing capability of these membranes is attributed to the reinforcing effect resulted from the interaction between fillers and the polymer [18].

3.5. Electrochemical property

Ionic conductivity describes the ability of polymer membrane to conduct Li^+ in lithium-ion battery system. For the application in real lithium ion batteries, the separator/electrolyte system must have high ionic conductivity. Table 4 exhibits ionic conductivity of polymer membranes before and after immersing into 1 M LiClO_4 – PC electrolyte solution for 24 hours.

Interestingly both results exhibit similar trends for all membrane samples with optimum ionic conductivity is obtained by polymer membrane with addition of 10% fly ash 300 meshes filler. The presence of fly ash fillers successfully enhances the ionic conductivity of polymer membrane electrolyte. The highest increase in ionic conductivity (3.03 mS cm^{-1}) is obtained for the membrane prepared with addition of 10% fly ash with 300 meshes. However, further increase in fly ash content decreases the ionic conductivity. Similar observation with different material was reported by Leo et al. [27] and Croce et al. [30]. They reported that maximum concentration of ceramic filler added to polymer in enhancing ion conductivity is generally within the range of 8 – 10 % polymer weight. For same concentration, addition of fly ash with smaller size generates higher conductivity. The reason for this phenomenon is that the smaller fly ash creates more conducting pathway that will improve the mobility of Li^+ ions to migration in the polymer electrolyte [31].

Table 4. Ion conductivity test results of various membranes

Fly ash concentration (% wt.)	Size of fly ash (mesh)	Ionic conductivity before immersion (mS cm^{-1})	Ionic conductivity after immersion (mS cm^{-1})
0	-	0.31	1.8
5	150	0.35	2.52
5	300	0.38	2.56
10	150	0.65	2.82
10	300	0.8	3.03
15	150	0.49	2.71
15	300	0.46	2.66

High ionic conductivity of electrolyte membranes resulted from this study is affected by several factors, such as crystallinity, porosity, uptake solution, leakage, and certainly different concentration and size of filler added to membrane which will be discussed hereinafter. Adopting from Dissanayake et al. [31], the increase in ionic conductivity is attributed to the presence of alumina in fly ash. Lewis acid–base type oxygen and OH surface groups on alumina grains in fly ash interact with cations and anions, which will provide additional sites creating favorable high conducting pathways in the vicinity of grains for the migration of ions. These high conducting pathways enhance the mobility of Li^+ ions to migrate from anode to cathode as conversely. Fly ash

particles act as conducting medium or pathway in membrane composite polymer. The increase in conductivity will depend on the conductivity of fly ash itself, the density of fly ash in polymer membrane and the distribution fly ash particles in polymer membrane. At low concentration of fly ash yielding low density the increase in ionic conductivity can clearly be observed. The ionic conductivity increases as the fly ash concentration was increased. However at high concentration of fly ash the ionic conductivity decreases. This phenomenon is also observed by previous works using alumina grain as fillers for polymer electrolyte [31]. In this study, the decrease in ionic conductivity at high fly ash content is due to the blocking effect or the geometrical constrictions imposed by the more abundant fly ash grains.

The amorphous structure has an advantage compared to crystalline structure because it will be easier to be swollen by electrolyte solution as result from higher affinity between polymer matrix and liquid electrolyte. In addition, the amorphous flexible polymer matrix is favorable in increasing space for electrolyte solution, so that much Li^+ can be induced [16]. However, it is believed that there should be an optimum value of degree of amorphousness. Ionic conductivity increases as the electrolyte solution increases the mobility and the concentration of the ionic charge carriers [16]. After soaking more electrolyte solution, leakage has to be hindered to keep electrolyte solution lying in polymer. In this work, the leakage of electrolyte solution decreases with addition of fly ash particles.

4. Conclusions

Fly ash/PVdF-PAN composite polymer electrolyte membranes for Li-ion batteries was prepared with the addition of fly ash. Membrane characterizations including porosity, crystallinity, electrolyte uptake solution and leakage have also been performed. It has been shown that incorporating fly ash fillers into PVdF-PAN polymer membrane has successfully enhanced mechanical and ionic conductivity of polymer electrolyte, which is generally optimum for the membrane prepared with addition of 10% fly ash and particle size 300 meshes. The mechanical properties improve considerably with fly ash addition. A maximum tensile strength of 16.36 MPa was found, which was more than twice higher than that of the pristine PVdF-PAN membrane. Ionic conductivity of PVdF-PAN membrane was improved by addition of fly ash fillers. High ionic conductivity of 0.8 mS cm^{-1} and 3.03 mS cm^{-1} , which is greater than of 0.31 mS cm^{-1} and 1.8 mS cm^{-1} of PVdF-PAN membranes without fillers was gained before and after immersed in electrolyte solution, respectively. These results are suitable for Li-ion battery application.

Acknowledgements

The authors gratefully acknowledge the Directorate General of Higher Education, Indonesia (DIKTI), the Republic of Indonesia for the financial supports of this research. RM would like to thank the Ministry of Education of Culture, the Republic of Indonesia for his Master scholarship.

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