Conductivity Studies of Conducting Liquid Crystal Polymer with Low 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid Content

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ABSTRACT

Low content of conducting block which 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid (AMPSA) are synthesized with liquid crystal polymer which is Methyl Methacrylate (MMA) with ratio sample 10%, 25% and 50% of AMPSA to the MMA. This sample was synthesized with randomly polymerized structure and was demonstrated by Electrochemical Impedance Spectroscopy Hioki 3532-50 (EIS) for conductivity studies. The conductivities of the sample increases with increasing of ratio AMPSA to the MMA at temperature range 70°C and 80°C. Based on the study of dc conductivity versus 1000/T, the temperature dependency with conductivity using of Arrhenius plot and Vogele-Tammanne-Fulcher (VTF) model are discussed.

Keywords— 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid, Methyl Methacrylate, Electrochemical Impedance Spectroscopy, Vogele-Tammanne-Fulcher.

1.0 INTRODUCTION

Recently, over these five decades liquid crystalline (LC) polymer have been an interest of the industrialists after the found of liquid crystalline (LC) state of synthetic rigid-rod polymer. The well-developed LC polymer structure are believed to be a beneficial application in wide range field of new devices, energy, environment, resources and biotechnologies [1].

LC been discovered by its ability to improve the transport of ion and solvent in polymeric membrane. Thus, it can be applied as electrolyte for fuel cell for example Direct Methanol Fuel Cell (DMFC) [2]. Out dated, the restriction that still present in DMFC such as the crossover phenomenon must be clear up for their application at a huge scale. This happen when methanol diffuses from anode through the electrolyte and react with oxygen at the cathode which lead to problem of mixed potential and reduction in the DMFC cell efficiency [2]. The membrane that usually used in the DMFC is Nafion. Whenever Nafion is used, it can enhance proton conductivity in the DMFC when water and methanol are rapidly absorbed through the hydrophilic region by filling the ionic clusters and forming a network of pools and channels [3]. Absorbing to much water make the uncontrolled phase separation happen in Nafion, thus it develops excessive swelling and methanol crossover in DMFC [2]. Due this limitation, several efforts had been made to find an alternative for Nafion for better application such as by synthesis new LC polymer with conducting block which are 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid (AMPSA)

In this research focus on how the liquid crystal polymer which are Methyl Methacrylate (MMA) that synthesized randomly polymerization with low 2-Acrylamido -2- Methyl-1-Propanesulfonic Acid (AMPSA) as conducting block will affect the conductivity either will so that it can be used as electrolyte for further application. The objective of this research is to study the conductivity of the polymer with different ratio of conductivity block and liquid crystal block and to determine optimal conductivity based on polymer structure

2.0 METHODOLOGY

2.1 *Material*

Liquid crystal that will be used is MMA and AMPSA will be conducting element or block that are synthesize together previously. Polymer was synthesizing with different ratio of these material which low ratio conducting element of AMPSA to liquid crystal MMA. There are three different ratios of the AMPSA: MMA that been synthesis which are 10%, 25% and 50% with random or radical polymerization structure.

2.2 *Sample Preparation*

In this research three set of samples are prepared. A pair of stainless steel discs were used as electrode and samples were placed sandwiched between two discs. Three sheet of Teflon paper were cut into plate electrode size and a hole are punch randomly in size at the centre of the Teflon paper. Due to different sizes of hole, it required to measure the diameter of hole at the centre of the paper by using digital calliper. The purpose of punch the hole at the centre to get the accurate diameter sample AMPSA-MMA that placed in between on the pair of electrode disc.

All three of Teflon paper are placed in between two discs electrodes. And those three set of disc electrode with Teflon paper thickness are measure before sample AMPSA-MMA are place on it. Then the sample 10%, 25% and 50% of AMPSA-MMA are placed evenly on the centre of the place. This step is prepared on the hot plate so that the AMPSA-MMA melt and the material and be spread evenly in the hole that had been made. Then the sample are sandwich together within two disc electrodes and the thickness are measured once again by using digital calliper.

2.3 *Electrochemical Impedance Spectroscopy (EIS)*

Electrochemical Impedance Spectroscopy Hioki 3532-50 is used to measure the conductivity of the liquid crystal polymer with low conducting material which is AMPSA-MMA. The temperature used for the measurements are from 30°C to 100°C with plus minus 0.1°C. The sample set of sandwiched plate electrode with diameter range within 12.5 to 8.0 mm and thickness in ranger 0.07 to 0.13 mm are placed in the chamber. The conductivity data are taken at 10°C temperature interval. Each sample will be run about two-time heating and one-time cooling with the frequency from 50Hz to 1MHz.

3.0 RESULTS AND DISCUSSION

3.1 *Conductivity*

Table 4.1 below shown are summarized the all result for each sample of 10%, 25% and 50% ratio AMPSA to MMA. From the table the highlighted column has the highest and the average for carrier who each sample at specific temperature where, 10% sample at 70°C and 80°C for both 25% and 50% conductivity among the run times for each sample.

Table 1 Summarized table on the highest conductivity for all three-run time (first heating, cooling and second heating) on each sample ratio AMPSA to MMA

	First heating (Scm^{-1}) 10^{-6}	Cooling (Scm^{-1}) 10^{-6}	Second heating 10^{-6} (Scm^{-1})	Average (Scm^{-1}) 10^{-6}
10%	0.0040	0.0034	0.0025	0.010
25%	173.69	132.92	56.52	363.1
50%	835.74	1589.88	497.85	2923.5

Based on all the result from each sample which are 10%, 25% and 50% being discuss, graph on log conductivity versus frequency in Figure 1 below are plotted based on the highest data from the Table 1 for each sample. From the table also, the average for the three-run (first heating, cooling and second heating) time are calculated for each sample ratio. Based on the table the highest average of conductivity from all the sample that had been synthesized with different ratio of conducting block to liquid crystal polymer can be determined. Sample of 50% ratio AMPSA to MMA have the highest conductivity among all sample which is $2923.460x10^{-6}$ Scm^{-1} follow with 25% ratio sample and 10% ratio sample with $363.122x10^{-6}Scm^{-1}$ and 0.0099x 10^{-6} Scm^{-1}.

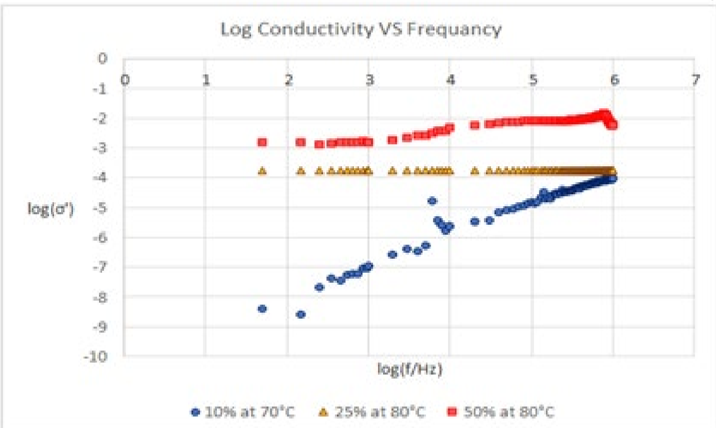


Figure 1Comparison Graph between Sample 10%, 25% and 50% ratio AMPSA:MMA with Various Frequency on the Conductivity.

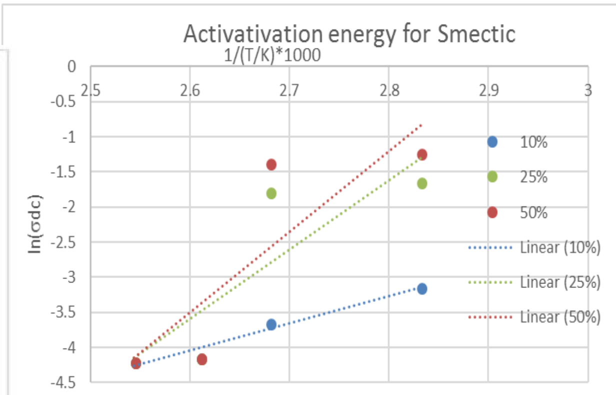
From the previous studies, state that the conductivity increases with the increasing ratio of conducting block which is AMPSA in the polymer chain to VTri [4]. Based on the previous study and compared with Figure 1 it can be conclude that in this conductivity studies of AMPSA also have similar result as increasing the ratio of AMPSA to the MMA based on the Figure 4.7 from 10% to 50% shown the increasing of conductivity.

Besides that, from different previous study mention that, the low ratio of AMPSA to the copolymer where the sample are synthesized with 0.5%, 1% and 2% show that different conductivity for each sample where the higher ratio has higher conductivity but for low ratio sample the conductivity are very low thus expected transportation of proton are irrelevant [5]. Since in the low ratio of conducting block is 10% with very low conductivity which is 0.0099x 10^{-6} Scm^{-1} from the graph shown in Figure 4.2 that the conductivity curve was rapidly drop as increasing the frequency. Meanwhile, for the sample high ratio AMPSA to MMA which is 50% ratio shown in Figure 4.6 the well-developed (cooling run time) from the higher frequency to low frequency at temperature 70°C and have sudden drop at low frequency. This happen might be due to the electrode polarization at higher temperature [5].

Other than that, due to low ratio of the conducting block to liquid crystal block (AMPSA: MMA) it not suitable to be used in cell under higher temperature. This statement mentions as observation from each sample, for example for 50% ratio sample shown that the higher conductivity is at 70°C where at the highest temperature which is 100°C the conductivity are drop rapidly. Same goes to the 10% and 25% ratio sample where the highest conductivity is at 70°C and 80°C.

3.2 *Activation Energy*

Values of dc conductivity basically are important as it is one of the characteristic advantages during selection of solid polymer electrolytes in application of electrochemical device [6]. Data from the ac conductivity which are extrapolated linearly to zero frequency are used as estimation to get the dc conductivities of each sample in this study. The dc conductivity value is obtained from the Zmin in the real and imaginary ratio from the EIS which is plot of (Z'/Z''). In Figure 2 shown the temperature dependence of the conductivities AMPSA to MMA for each sample ratio which are 10%, 25% and 50% are compared with Arrhenius model. In the graph is observed between sematic region with temperature range from 70°C to 100°C. since the Arrhenius plot for this study are nonlinear, the dependency of temperature to the conductivity data can precisely describe by VTF model.



ccording to the previous study state that most of the polar mer used in preparation of polymer electrolyte are crystalline polymer for example containing both crystal and phous phases [6]. Based on the Figure 2 shown that the curve rrhenius plot for VTF model has been attributed to the nce of strong inter-relation between the ionic motion and polymer segmental relaxation for each sample of ratio. This also implies that the polymer segmental relaxation and ionic motion are well coupled with each other. Table 2 below represent the activation energy for each of the sample ratio.

Table 2 below represent the activation energy for each of the sample ratio 10%, 25% and 50% of AMPSA to MMA

Smectic			
Regions	**100>T>70**		
Paremeters	10%	25%	50%
c	-14.20	-29.38	-33.43
m	3.91	9.92	11.51
Ea	32.47	82.42	95.66

* from linear line c indicate intercept, m is gradient and Ea is activation energy.

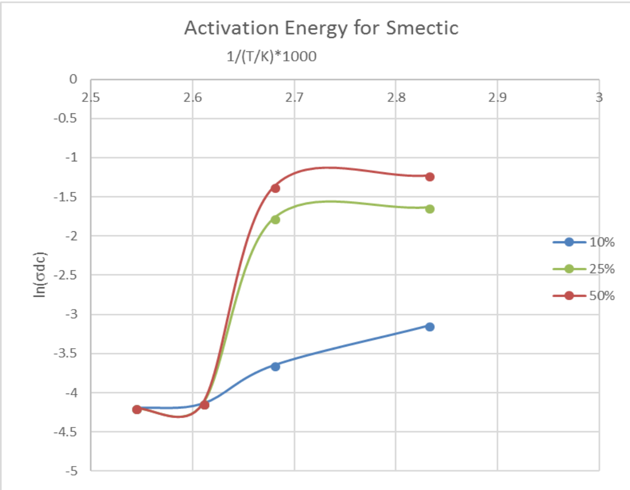


Figure 4Temperature dependence of dc conductivity of the sample 10%, 25% and 50% ratio of AMPSA to MMA obtained from the extrapolation of ac conductivity data

Conclusion

This study is done to find the alternative to find an alternative for Nafion for better application such as by synthesis new LC polymer Methyl Methacrylate with low content of conducting block which is AMPSA where the conductivity is been study to meet the need of economic membrane used in DMFC. As in this study the conductivity of the sample is increasing by increasing the ratio of AMPSA to MMA sample which are from 10%, 25% to 50%. Other than that, the low ratio of AMPSA also not suitable to be used in cell with higher temperature as each sample of ratio have highest conductivity at temperature in range 70°C to 80°C.

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References

[1] Kato, T., Uchida, J., Ichikawa, T., & Soberats, B. (2017). Functional liquid-crystalline polymers and supramolecular liquid crystals. *Polymer Journal*. doi:10.1038/pj.2017.55

[2] Martínez-Felipe, A. (2011). Liquid crystal polymers and ionomers for membrane applications. *Liquid Crystals, 38*(11-12), 1607-1626. doi:10.1080/02678292.2011.624201

[3] Mauritz, K. A., & Moore, R. B. (2004). State of Understanding of Nafion. *Chemical Reviews, 104*(10), 4535-4586. doi:10.1021/cr0207123

[4] Çelik, S. Ü., & Bozkurt, A. (2010). The synthesis and proton-conducting properties of the copolymers based on 1-vinyl-1,2,4-triazole and 2-acrylamido-2-methyl-1-propanesulfonic acid. *Solid State Ionics, 181*(11), 525-530. doi:https://doi.org/10.1016/j.ssi.2010.02.019

[5] Erdemi, H., Bozkurt, A., & Meyer, W. H. (2004). PAMPSA–IM based proton conducting polymer electrolytes. *Synthetic Metals, 143*(1), 133-138. doi:https://doi.org/10.1016/j.synthmet.2003.10.022

[6] Aziz, S. B., Woo, T. J., Kadir, M. F. Z., & Ahmed, H. M. (2018). A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices, 3*(1), 1-17. doi:https://doi.org/10.1016/j.jsamd.2018.01.002