



Physical and Conductivity Studies of Plasticised Methyl Cellulose-Lithium Triflate based Polymer Electrolyte

Nursyahida Sahli^{1*}, Nordiana Nabilla Ramly¹, Muhd Zu Azhan Yahya²
and Ab Malik Marwan Ali^{1,3}

¹Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

²Faculty of Defence Science and Technology, Universiti Pertahanan Nasional Malaysia (UPNM),
Kem Sungai Besi, 57000, Kuala Lumpur, Malaysia

³Institute of Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

ABSTRACT

Solid polymer electrolyte based on methyl cellulose (MC)-lithium triflate (LiCF_3SO_3) plasticised with ethylene carbonate (EC) was prepared using solution cast technique. The X-ray diffraction (XRD) studies proved that the amorphous nature of the electrolyte systems was increases due to the addition of salt and plasticiser. The improved surface morphology of plasticised polymer system ensures it has good electrode-electrolyte contact during performance testing. The polymer electrolyte was found to have high thermal stability indicating that the electrolyte can be used at higher temperature. The ionic conductivity increased up to $1.24 \times 10^{-4} \text{ S cm}^{-1}$ at optimum amount of EC plasticiser associated to the effect of plasticiser that initially leads to the formation of Li^+ -EC complex. Consequently, it reduces the fraction of polymer- Li^+ complex which contributes to the increase of the segmental chain flexibility in the plasticized system. Temperature dependent studies indicate ionic conductivity increase due to the temperature increase and is in line with Arrhenius behaviour pattern. An activation energy of 0.26 eV at highest conductivity sample was obtained. The addition of plasticiser lowers the activation energy thus increasing the ion mobility of the system and contributing to ionic conductivity increment. The plasticization method is a promising means to dealing with the solid polymer electrolyte problem and producing electrolytes that meet the needs of electrochemical devices.

Keywords: Lithium triflate, ethylene carbonate, impedance spectroscopy, X-ray diffraction

ARTICLE INFO

Article history:

Received: 28 September 2016

Accepted: 03 February 2017

E-mail addresses:

syahidasahli@gmail.com (Nursyahida Sahli),

dianaramly@gmail.com (Nordiana Nabilla Ramly),

mzay@upnm.edu.my (Muhd Zu Azhan Yahya),

ammali@salam.uitm.edu.my (Ab Malik Marwan Ali)

*Corresponding Author

INTRODUCTION

Solid polymer electrolytes (SPEs) has great potential in electrical energy storage systems such as batteries, super capacitors, fuel cell and solar cell as the alternative sources

(Dissanayake et al., 2002; Malathi et al., 2010; Shukur et al., 2013). This electrolyte also is known for its ability to overcome the leakage problem of toxic liquid electrolyte, high energy density, good thermal stability and high conductivity (Gopalan et al., 2008; Johan et al., 2013). However, the conductivity achievement and electrode-electrolyte contact still needs to be improved for commercial purposes.

The plasticization method is a promising method to modify the SPE beside formation of cross-linked network (Wetjen et al., 2013), copolymerization (Li et al., 2013), and insertion of ceramic filler (Tan et al., 2007). It involves the introduction of plasticiser into SPEs system which also known as gel polymer electrolytes (GPEs). Several plasticiser such as propylene carbonate (PC) and ethylene carbonate (EC) are widely used in polymer electrolyte (Ali et al., 2011; Mahmud et al., 2012).

Pradhan et al. (2010) in their work reported that the conductivity of SPE increases with the addition of plasticiser due to the lowering of glass transition temperature and increasing the amorphous phase of the polymer. In the present study, EC is selected as the plasticiser due to its low molecular weight and higher dielectric constant ($\epsilon = 89.6$) compare to the polymer host (Ramesh et al., 2011). The high dielectric constant of the plasticiser helps the ions to have better dissociations. The study investigates the physical and electrical performance in producing better polymer electrolyte with plasticiser content.

METHOD

Polymer electrolytes consisting of methylcellulose (MC) as polymer host, lithium triflate (LiCF_3SO_3 or LiTf) as a doping salt and EC as plasticiser was prepared using solution cast technique. Dimethyl formamide (DMF) was used as a solvent to dissolve all the materials. Prior to the preparation of polymer-salt solution the LiCF_3SO_3 salt was dried at 100°C in order to eliminate the excessive water. 1 g of MC and lithium salt were dissolved separately in DMF and then were mixed together in a Scott bottle. The mixture was stirred for about 24 hours before casting on Teflon petri dish to let the solvent evaporate slowly until the polymer-salt film form. The procedure repeated with different stoichiometric ratios of lithium salt. For GPEs systems, the sample with the highest ionic conductivity was mixed with different weight percent of EC using the similar procedures. The free-standing film forms were obtained through slowly drying process inside a vacuum oven at temperature of 60°C . All the samples were prepared at room temperature and stored in desiccators for further use. The thicknesses of the films were between 0.1 mm and 0.2 mm.

For structural analysis, X-ray diffraction pattern of the films were recorded by PAN Analytical X-ray diffractometer with $\text{CuK}\alpha$ radiation wavelength (1.54056 \AA) in the 2θ angle range between 10° to 40° with scanning rate 5° min^{-1} . Environmental scanning electron microscopy (ESEM) was used to determine the morphology of the samples with $5000\times$ scanning magnification. The thermal studies were performed using thermogravimetric analysis (TGA) at heating temperature from 25°C to 500°C , and conductivity measured by AC impedance spectroscopy studies using HIOKI 3531 Z Bridge at frequency range between 100 Hz and 1

MHz at amplitude 10mV. The polymer electrolytes were sandwiched between two stainless steel blocking electrodes with humidity controlled. The conductivity-temperature dependence study was conducted in the temperature range 303 K to 363 K.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractograms of pure MC film, pure LiCF_3SO_3 , MC with 30wt.% LiCF_3SO_3 and MC- LiCF_3SO_3 with 40wt.% EC content. The broad peaks of pure MC appeared between $2\theta = 10^\circ$ and 30° correlated to the crystalline nature of methylcellulose known as amorphous hump. The pattern shows that the amorphous character of the samples increased as the crystalline peaks decreased gradually and their width began to broaden following the addition of lithium salt (Caruso et al., 2002). The crystalline peak of pure lithium which exhibited at $2\theta = 16.27^\circ, 19.5^\circ, 22.24^\circ, 31.98^\circ, 39.65^\circ$ (Figure 1(d)) appeared to disappear in the polymer-salt system (Figure 1b) indicating the complete dissolution of lithium salt in the polymer system (Ahmad et al., 2011). Figure 1c shows the X-ray diffractogram of plasticized film is similar with the X-ray diffractogram of polymer salted film. The crystalline nature of this film was decreased compared to the pristine polymer sample indicates that the addition of EC increase the amorphous domain of MC- LiCF_3SO_3 polymer matrix. The reduction in crystallinity could explain increases in conductivity, suggesting crystallinity and conductivity are related in the sample (Johan et al., 2011).

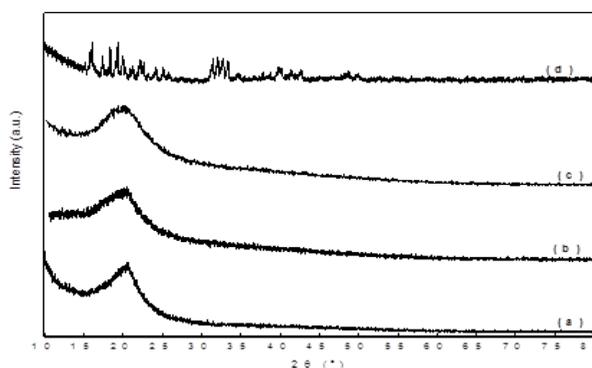


Figure 1. XRD pattern of (a) Pure MC; (b) MC-30wt% LiCF_3SO_3 ; (c) MC- LiCF_3SO_3 -40wt% EC; and (d) Pure LiCF_3SO_3

Figure 2 shows the surface morphology (ESEM) of pure MC film, polymer salt system and polymer salt-plasticiser system. The results show pure MC image has rough wrinkles surface with micro-pores. The addition of lithium salt onto the MC polymer in Figure 2(b) shows a reduction of the roughness of the surface structure while the XRD analysis shows the amorphous hump became less sharp and broadened in polymer salt system implying that the amorphousness phase in the electrolyte has increased. Due to this observation, it is suggested that the increase of the amorphousness phase in MC polymer is associated with the smooth surface morphology of the polymer electrolyte as a result of the interaction of ether oxygen of

MC and Li^+ ions (Johan et al., 2011). In Figure 2(c) it can be noticed that the surface morphology of the plasticised polymer-salt appears very smooth, dense and absent of pores. Predictably, larger plasticisers were entrapped within the polymer matrix thus increase the flexibility of the segmental motion of where influenced in the transporting of charge carriers and successfully improved the surface layer of the electrolyte. This result ensures good electrode-electrolyte contact and impedance spectroscopy characterization and device applications (Shukur et al., 2014).

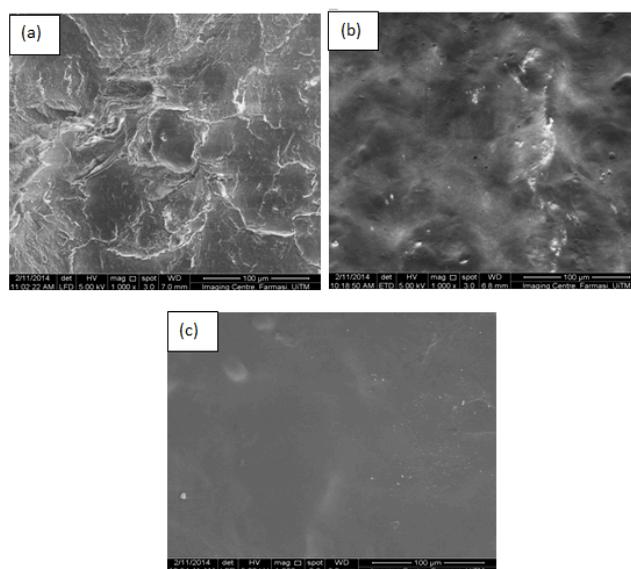


Figure 2. FESEM image (a) Pure MC; (b) MC-30wt% LiCF_3SO_3 ; and (c) MC- LiCF_3SO_3 -40wt% EC complexes

The thermogravimetric curve at different polymer electrolyte systems shows in Figure 3. The initial degradation of the % weight loss at temperature below $100\text{ m}^\circ\text{C}$ is due to the removal of moisture, transition of the sample or volatilization of small molecules and/or monomers (Guirguis & Moselhey, 2012; Ramesh & Yi, 2009). For pure MC (Figure 3(a)) no further weight loss is observed until decomposition commenced at approximately 302.2°C before drastically decline. This indicates that the film preparation method was stable at up to 300°C . The total weight loss for pure MC film is 83.18%. In MC-30wt.% LiCF_3SO_3 system (Figure 3(b)) show steps of temperature degradation. The film constantly stable from 130°C to 250°C until second degradation occurs at 256.7°C . The degradation begins from 256.7°C to 302.1°C might be cause by decomposition of MC. This remark that the thermal stability for sample containing MC-30wt.% LiCF_3SO_3 stable up to 250°C before decomposition. Finally, degradation from 302.1°C to 499°C indicates the main thermal degradation of MC and LiCF_3SO_3 complexes. Thermal stability with the presence of LiCF_3SO_3 reduces the thermal stability of MC from 300°C to 256.7°C . This may be attributable to the weak interaction between MC and LiCF_3SO_3 caused the disruption in the complexes proved by FTIR results from previous studies (Sahli

& Ali, 2012). The addition of EC plasticiser on polymer-salt system (Figure 3(c)) shows the thermal stability increased where the major decomposition temperature for the second stage occurs at 269.9°C. The final degradation at 421°C to 500°C with the mass loss of 19.25% indicates the degradation of plasticizer EC. It is relevant to use MC based polymer electrolyte in electrochemical devices since the thermal stability is higher than 100°C.

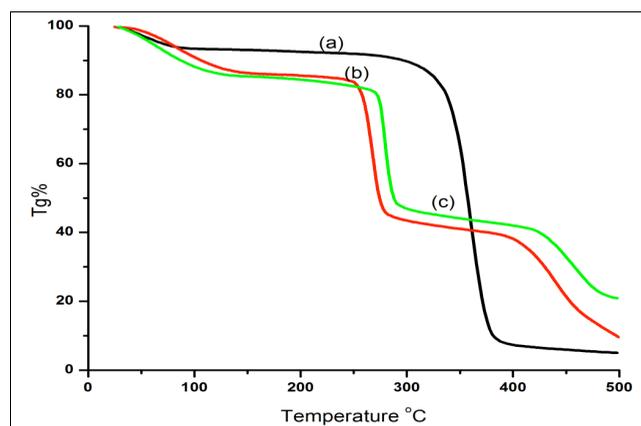


Figure 3. Thermograms for (a) Pure MC; (b) MC-30wt% LiCF₃SO₃ and (c) MC-LiCF₃SO₃-40wt% EC complexes

Figure 4 shows the ionic conductivity at variation wt.% of EC plasticiser in polymer electrolyte system. It can be observed that the highest ionic conductivity is $1.24 \times 10^{-4} \text{ S cm}^{-1}$ for 40 wt.% EC at room temperature. This phenomenon can be explained by the relatively low viscosity of the plasticiser which decreases the local viscosity around the charge transporting ion thereby increasing ionic mobility. The high dielectric constant of the plasticiser interrupts the coulombic force between the anions and cations of the salt contributed to the salt dissociation in the system therefore more free Li⁺ ions are produced (Saikia et al., 2008). The addition of plasticiser initially leads to the formation of Li⁺-EC complex which will reduce the fraction of polymer-Li⁺ complex. The flexibility of polymer chains will increase and contribute to improvement in conductivity.

Figure 5 represents the temperature dependence measurement for unplasticised polymer-salt and plasticized polymer-salt system at highest conductivity. The $\log \sigma$ versus $1000/T$ plot shows that the conductivity for both systems increases with increases in temperature, when a small amount of space surrounding its own volume is created through which ionic motion can take place and thereby increase conductivity. A similar tendency can be observed with ionic crystal where the ions jump into neighbouring vacant sites and increases conductivity when the temperature is raised. The regression values are near to unity indicating ion transport in the temperature dependence system follows the Arrhenius rules shown below Equation (1).

$$\sigma(T) = \sigma_0 \exp(-E_a/kT) \quad [1]$$

Where σ_0 is the exponential factor, E_a is the activation energy, K is the Boltzmann constant and T is the absolute temperature. The activation energy, E_a is the energy required for an ion to begin movement which calculated from the slope of the $\log \sigma$ versus $1000/T$ plot. The activation energies at the highest conducting samples for unplasticised and plasticized of the MC-based systems are presented in Table 1. It shows that the electrolytes with high conductivity exhibit the E_a (Yap et al., 2012). This can explained that in plasticized system the sufficient energy of ion is lower for the ion to transfer from the donor site to another thus leading increase the ion mobility (Johan et al., 2011).

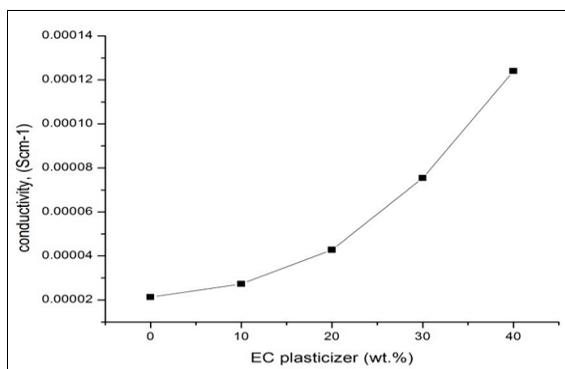


Figure 4. The conductivity plot of GPE system at different concentration of plasticiser at 303 K

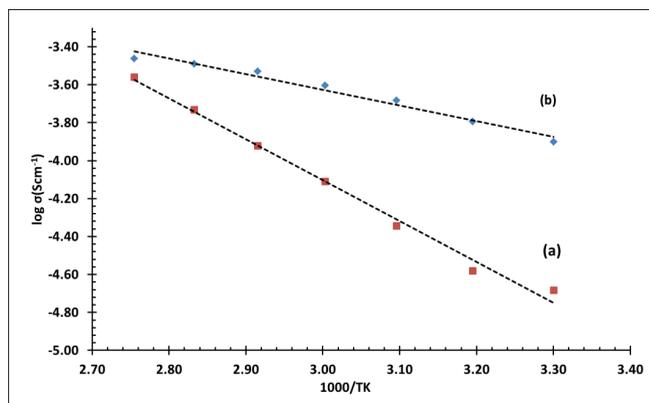


Figure 5. Temperature dependence of ionic conductivity for (a) MC-30wt% LiCF_3SO_3 ; and (b) MC- LiCF_3SO_3 -40wt% EC at 303-363 K

Table 1

The activation energy, E_a values for the highest conductivities of MC-30wt.% LiCF_3SO_3 and MC- LiCF_3SO_3 -40wt.% EC

Electrolyte	Conductivity, σ (S cm ⁻¹)	Activation energy, E_a (eV)
MC- LiCF_3SO_3	2.13×10^{-5}	0.68
MC- LiCF_3SO_3 -EC	1.24×10^{-4}	0.26

CONCLUSION

Polymer electrolytes consisting of MC-LiCF₃SO₃-EC have successfully prepared and investigated showed good thermal stability at high temperature. The XRD proved that by reducing crystallinity ionic conductivity can be enhanced as it has been noted to increase with rises in temperature increases.

ACKNOWLEDGEMENTS

The authors are grateful for financial assistance from the Ministry of Higher Education (MOHE) under the RAGS grant 600-RMI/RAGS 5/3 (12/2012) and to the Faculty of Applied Sciences and Institute of Science, Universiti Teknologi MARA for providing facilities.

REFERENCES

- Ahmad, A., Isa, K. B. M., & Osman, Z. (2011). Conductivity and Structural Studies of Plasticized Polyacrylonitrile (PAN) – Lithium Triflate Polymer Electrolyte Films. *Sains Malaysiana*, 40(7), 691–694.
- Ali, R. M., Harun, N. I., Ali, A. M. M., & Yahya, M. Z. A. (2011). Conductivity studies on plasticised cellulose acetate–ammonium iodide based polymer electrolytes. *Materials Research Innovations*, 15(2), 39–42.
- Caruso, T., Capoleoni, S., Cazzanelli, E., Agostino, R. G., Villano, P., & Passerini, S. (2002). Characterization of PEO-Lithium Triflate Polymer Electrolytes: Conductivity, DSC and Raman Investigations. *Ionic*, 8, 36–43.
- Dissanayake, M. A. K. ., Bandara, L. R. . K., Bokalawala, R. S., Jayathilaka, P. A. R. ., Ileperuma, O. ., & Somasundaram, S. (2002). A novel gel polymer electrolyte based on polyacrylonitrile (PAN) and its application in a solar cell. *Material Research Buletin*, 37, 867–874.
- Gopalan, A., Santhosh, P., Manesh, K., Nho, J., Kim, S., Hwang, C., & Lee, K. (2008). Development of electrospun PVdF–PAN membrane-based polymer electrolytes for lithium batteries. *Journal of Membrane Science*, 325(2), 683–690.
- Guirguis, O. W., & Moselhey, M. T. H. (2012). Thermal and structural studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends. *Natural Science*, 4(1), 57–67.
- Johan, M. R., Shy, O. H., Ibrahim, S., Mohd Yassin, S. M., & Hui, T. Y. (2011). Effects of Al₂O₃ nanofiller and EC plasticizer on the ionic conductivity enhancement of solid PEO–LiCF₃SO₃ solid polymer electrolyte. *Solid State Ionics*, 196(1), 41–47.
- Kumar Kiran, K., Ravi, M., Pavani, Y., Bhavani, S., Sharma, A., & Narasimha Rao, V. V. . (2012). Electrical conduction mechanism in NaCl complexed PEO/PVP polymer blend electrolytes. *Journal of Non-Crystalline Solids*, 358(23), 3205–3211.
- Li, L., Wang, J., Yang, P., Guo, S., Wang, H., Yang, X., ... Wu, B. (2013). Preparation and characterization of gel polymer electrolytes containing N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ionic liquid for lithium ion batteries. *Electrochimica Acta*, 88, 147–156.

- Mahmud, Z. S., Adam, N. I., Zaki, N. H. M., Ali, A. M. M., & Yahya, M. Z. A. (2012). Conductivity and optical studies of plasticized polymer electrolytes based on 49% PMMA-grafted natural rubber. *2012 IEEE Symposium on Business, Engineering and Industrial Applications*, 504–508.
- Malathi, J., Kumaravadivel, M., Brahmanandhan, G. M., Hema, M., Baskaran, R., & Selvasekarapandian, S. (2010). Structural, thermal and electrical properties of PVA–LiCF₃SO₃ polymer electrolyte. *Journal of Non-Crystalline Solids*, 356, 3377–2281.
- Pradhan, D. K., Samantaray, B. K., Choudhary, R. N. P., Karan, N. K., Thomas, R., & Katiyar, R. S. (2010). Effect of plasticizer on structural and electrical properties of nanocomposite solid polymer electrolytes. *Ionics*, 17(2), 127–134.
- Ramesh, S., Shanti, R., & Durairaj, R. (2011). Effect of ethylene carbonate in poly (methyl methacrylate)-lithium tetraborate based polymer electrolytes. *Journal of Non-Crystalline Solids*, 357(5), 1357–1363.
- Ramesh, S., & Yi, L. J. (2009). Structural, thermal, and conductivity studies of high molecular weight poly(vinylchloride)-lithium triflate polymer electrolyte plasticized by dibutyl phthalate. *Ionics*, 15(6), 725–730.
- Sahli, N., & Ali, A. M. M. (2012). Effect of lithium triflate salt concentration in methyl cellulose-based solid polymer electrolytes. *Humanities, Science and Engineering (CHUSER), 2012 IEEE Colloquium on*, 739 – 742.
- Saikia, D., Chen-Yang, Y. W., Chen, Y. T., Li, Y. K., & Lin, S. I. (2008). Investigation of ionic conductivity of composite gel polymer electrolyte membranes based on P(VDF-HFP), LiClO₄ and silica aerogel for lithium ion battery. *Desalination*, 234(1-3), 24–32.
- Shukur, M. F., Ithnin, R., Illias, H. a., & Kadir, M. F. Z. (2013). Proton conducting polymer electrolyte based on plasticized chitosan–PEO blend and application in electrochemical devices. *Optical Materials*, 35(10), 1834–1841.
- Shukur, M. F., Ithnin, R., & Kadir, M. F. Z. (2014). Electrical characterization of corn starch-LiOAc electrolytes and application in electrochemical double layer capacitor. *Electrochimica Acta*, 136, 204–216.
- Tan, C. G., Siew, W. O., Pang, W. L., Osman, Z., & Chew, K. W. (2007). The effects of ceramic fillers on the PMMA-based polymer electrolyte systems. *Ionics*, 13(5), 361–364.
- Wetjen, M., Kim, G.-T., Joost, M., Winter, M., & Passerini, S. (2013). Temperature dependence of electrochemical properties of cross-linked poly(ethylene oxide)–lithium bis(trifluoromethanesulfonyl) imide–N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide solid polymer electrolytes for lithium batteries. *Electrochimica Acta*, 87, 779–787.
- Yap, K. S., Teo, L. P., Sim, L. N., Majid, S. R., & Arof, A. K. (2012). Investigation on dielectric relaxation of PMMA-grafted natural rubber incorporated with LiCF₃SO₃. *Physica B: Condensed Matter*, 407(13), 2421–2428.