The Investigation on Ionic Conduction of PEMA Based Solid Polymer Electrolytes

Shahrul Amir^{1, a}, Nor Sabirin Mohamed^{2, b} and Ri Hanum Yahaya Subban^{3, c}

¹Department of Engineering, Center for Foundation Studies

International Islamic University of Malaysia, 46350 Petaling Jaya, Selangor, Malaysia ²Center for Foundation Studies in Science, University of Malaya, 50603 Kuala Lumpur, Malaysia ³Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia ^ajcv90210@yahoo.com, ^bnsabirin@um.edu.my, ^crihanum43@salam.uitm.edu.my

Keywords: polymer electrolytes. conductivity, XRD, scherrer length, dielectric constant

Abstract. Solid polymer electrolytes comprising of various weight ratios of poly(ethyl methacrylate) (PEMA) and lithium perchlorate (LiClO₄) salt were prepared via solution casting technique using N,N-Dimethylformamide (DMF) as the solvent. The conductivity values of the electrolytes were determined utilizing Solatron 1260. The highest conductivity obtained is in the order of 10^{-6} S cm⁻¹. Structural properties of the electrolytes were investigated by X-ray diffraction and the results show that the highest conducting film is the most amorphous.

Introduction

Polymer is a material constructed of a large number of molecules that is formed from the repetition of small and simple chemical units called monomer bonded by covalent bonds. Most polymers have no ability to conduct electricity. Besides its poor electrical conductivity property, for the last five decades, ion conducting polymers has been synthesized via dissolving inorganic salt into its matrix. Polymer electrolytes possess various advantages such as solvent free condition, structurally stable, easy for any process and mobileable [1]. Various kinds of polymers have been chosen as host such as PEO [2], PPO [3], PVA [4,5], PVC [6], PVDF [7] and PMMA [8]. In this work, the potential of PEMA as a polymer host is investigated. LiClO₄ is added as the doping salt. PEMA was chosen as host as it exists in amorphous form [9]. By incorporating LiClO₄ in to PEMA, it was hoped that the media for ion mobilities will be enhanced.

Experimental

Various weight percentages, wt% of LiClO₄ was dissolved into commercially available PEMA ($M_w = 215,000$) employing DMF as solvent. The films were cast using the solution casting method. The cast films were subjected to EIS (Solatron 1260) and XRD analysis (LabX XRD 6000) for impedance and structural studies respectively.

Results and Discussion

Fig. 1 depicts the X-Ray diffractograms of PEMA-LiClO₄ films at various concentrations. For pure PEMA, the XRD pattern obtained in this work is similar to that obtained by Rajendran et.al [10] that is a small peak appeared at $2\theta \approx 29.5^{\circ}$. PEMA-LiClO₄ diffractograms show a few peaks due to the presence of LiClO₄ and is prominent for the film with 30 wt% LiClO₄. Such observation is most possibly due to the uncomplexed salt or ion aggregation of the salt. For 30 wt% LiClO₄ the degree of uncomplexed salt or ion aggregation is the highest.



Functionalized and Sensing Materials



Fig. 1: X-ray diffractograms of PEMA with (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25 and (g) 30 wt% LiClO₄.

The Scherrer length, L, for every sample was determined using the equation

$$L = \frac{0.9\lambda}{\Delta 2\theta_{halfpeak} \sin(\frac{2\theta_{\max}}{2})}$$
(1)

where $\lambda = 1.5418$ Å and $\Delta 2\theta$ is the width at half maximum. In this work, Scherrer length was calculated using the peak at 29.5° and it shows that the sample with 20 wt % LiClO₄ has the smallest value as observed in Fig. 2. According to Hashmi et.al [11], the smaller the value of *L*, the more amorphous the sample is. Hence the most amorphous film has ratio of 80 wt % PEMA:20 wt % LiClO₄.



Fig. 2: Scherrer length for PEMA-LiClO₄ films

Graph of $\varepsilon_r - \log \omega$ depicted in Fig. 3 for all films. The dielectric constant is observed to rise sharply at low frequencies. According to Mohamed and co-worker [12], this indicates that electrode polarization and space charge effects had occurred.

(a)

click for feedback

Advanced Materials Research Vols. 93-94





Since ε_r is a reflection of the number of charge carriers present, hence it can be inferred that the sample with 20 wt % LiClO₄ has the highest number of charge carriers and is expected therefore to have the highest conductivity. This is supported by the graph shown in Fig. 4 which shows the variation of conductivity with salt concentration at room temperature. From Fig. 4, the highest conductivity obtained is 2.34 x 10⁻⁶ S cm⁻¹ for the sample with 20 wt % LiClO₄. This is comparable to the value of conductivity obtained for other dry polymer electrolytes reported in the literature [13,14,15]



Fig. 4: Conductivity variation with salt concentration of PEMA-LICIO₄ films

Fig. 4 also shows that the conductivity decreases for films with more than 20 wt % LiClO₄. This is attributed to the decrease in the fraction of amorphous region and decrease in the number of charge carriers as indicated in Fig. 2 and Fig. 3 respectively.

383

G click for feedback

Conclusion

The highest conductivity achieved in this work is $2.34 \times 10^{-6} \text{ Scm}^{-1}$ for the ratio of PEMA added with 20 wt % LiClO₄. There are still opportunities to increase the conductivity perhaps incorporating the existing samples with plasticizers or nanofillers. The results of this study indicate that PEMA has good potential to act as polymer host for electrolyte systems.

Acknowledgement

The authors are very thankful to Dr. Raihan Othman for his contribution in making the XRD analysis possible for this research project.

References

- [1] S. Ramesh, T. Winie and A.K. Arof: European Polymer Journal Vol 43 (2007), p. 1963
- [2] E.A. Reitman, M.L.R. Kaplan and J. Cava: Solid State Ionics Vol 25 (1987), p. 37
- [3] C. Roux, W. Gorecki, J. Y. Sanchez and E. Belorizky: Electrochem. Acta Vol 43 (1998), p. 1575
- [4] N. Srivastava, S. Chandra: Proceedings of 5th Asian Conference on Solid State Ionics 411, Kandy Sri Lanka (1996)
- [5] P.K. Shukla and S.L. Agrawal, Proceedings of the 6th Asian Conference on Solid State Ionics, New Delhi India (1998)
- [6] R.H.Y. Subban and A.K. Arof: Journal of New Materials for Electrochemical Systems Vol 6 (2003), p.197
- [7] N.S. Mohamed and A.K. Arof: Journal of Power Sources, Vol 132 (2004), p.229
- [8] A.M. Stephan, R. Thirunakaran, N.G. Reganathan, V. Sundaram, S. Pitchumani, N. Muniyandi, R. Gangadharan and P. Ramamoorthy: Journal of Power Sources Vol 81-82 (1999), p. 752
- [9] on http://www.polymerprocessing.com/polymers/PEMA.html
- [10] S. Rajendran, M. Ramesh Prabhu and M. Usha Rani: Journal of Power Sources Vol 180 (2008), p.880
- [11] S.A. Hashmi, Awalendra K. Thakur and H.M. Upadhyaya: European Polymer Journal Vol 34 (1998), p.1277
- [12] N.S. Mohamed and A.K.Arof: Journal of Power Sources Vol 132 (2004), p.229
- [13] K. Ito, Y. Tominaga, H. Ohno: Electrochimica Acta, Vol 42 (1997), p. 1561
- [14] G. Chiodelli, P. Ferloni, A. Magistris, M. Sanesi: Solid State Ionics, Vol 28-30, Part 2 (1988), p.1009
- [15] A.M.M. Ali, N.S. Mohamed, M.Z. Zakaria, A.K. Arof: Journal of Power Sources, Vol 66, (1997), p.169

