

Synthesis, Characterization, and Dielectric Studies of (1-x) PMMA: x PC: 10PVP: 5LiClO₄ Plasticized Blend Polymer Solid Electrolyte Systems

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Abstract - Plasticized blend polymer solid electrolytes (1-x) PMMA: x PC : 10 wt% PVP: 5 wt% LiClO₄ (where x = 10, 20, 30, 40 wt%) were synthesized according to their stoichiometric ratios. DC ionic conductivity study has been carried on four different polymer matrices and reported the maximum enhanced ionic conductivity is observed at a threshold combination of 70 wt% PMMA: 20 wt% PC: 10 wt% PVP: 5 wt% LiClO₄ polymer matrix. This could be attributed to the polymer matrix's segmental flexibility and increased Li⁺ ion mobility in the polymer matrix. Further dielectric studies are carried out and explained. The XRD patterns of all these solid electrolytes confirm an increase in the amorphous nature, increasing plasticizer PC wt%. DSC Thermograms has been carried out and explains the dependence of segmental flexibility of a polymer on T_g.

Keywords: Amorphous, Activation energy, Glass transition temperature, Segmental motion, Dielectric constant.

Introduction

Nowadays, rapid growth is taking place in portable electronic devices to develop electric vehicles, leading to the necessity of high energy stored secondary batteries [1]. Most Li-ion based batteries are available in a liquid state. The main disadvantage of these batteries is that leakage can cause fires and explosions, which can cause safety hazards [2,3]. These problems have been minimized in polymer-based solid

electrolyte systems, which play an important role in electrochemical equipment such as high energy density batteries, sensors, fuel cells, etc.; based on the type of polymers and their combinations, the solid polymer electrolytes can be divided into blended polymers, plasticized polymers, and composite polymers. Recently, more attempts have been made to enhance the ionic conductivity of the solid polymer electrolyte membranes, namely PEO-PMMA-LiClO₄-Silica Aerogel[4], PMMA-LiBF₄[5], PEG-EC-PEO-PMMA-AgNO₃[6], PEO-PVP-Li⁺-Ag [7], PEO-PMMA-PEG-Ag⁺ [8], PEO-PC-LiClO₄[9], EC-PC-PEO₉-LiTf-Al₂O₃[10], PEO-LiClO₄-Al₂O₃[11], PEO-LiClO₄[12], PEO-LiClO₄-ZnO[13], Al₂O₃-EC-PEO-LiCF₃SO₃[14], EC-PVC-LiNR50[15], EC(PEO)₉ LiCF₃SO₃[16], PMMA-LiClO₄-Clay[17] etc.. The applications of polymer-based solid electrolytes as secondary batteries have been motivated to select the present work. The polymers PMMA and PVP has been selected due to their good mechanical and thermal stability. The plasticizer is selected as PC due to having a high dielectric constant and low molecular weight, which helps in ion dissociation in the polymer matrix [28]. The current paper aims to study the Characterization and Impedance Spectroscopic properties of (1-x) PMMA: x PC: 10PVP: 5LiClO₄ Plasticized Blend Polymer Solid Electrolyte Systems.

Table-1 Polymer Designation and Activation energy of the polymer matrix

| Sl.No. | Polymer Matrix | Polymer Designation | Activation energy(eV) |
|--------|---|---------------------|-----------------------|
| 1 | 80Wt% PMMA : 10Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄ | PPSE-1 | 0.569eV |
| 2 | 70Wt% PMMA : 20Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄ | PPSE-2 | 0.392eV |
| 3 | 60Wt% PMMA : 30Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄ | PPSE-3 | 0.541eV |
| 4 | 50Wt% PMMA : 40Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄ | PPSE-4 | 0.569eV |



Materials and Methods

PMMA ($M_w \sim 1.2 \times 10^5$), PVP ($M_w \sim 3.6 \times 10^5$), PC ($M_w \sim 105$), DMF (N-N dimethylformamide), and $LiClO_4$ all the chemicals were procured from Sigma Aldrich India. Solid blended polymer electrolytes were synthesized using the solution cast method. In this technique, PMMA and PC were taken with different wt% keeping constant 10wt% of PVP and 5wt% of $LiClO_4$ where PMMA wt%:80, 70, 60, 50 PC wt%: 10,20,30,40 maintaining stoichiometric ratio and prepared blended polymer system (1-x) PMMA: x PC: 10 wt% PVP: 5 wt% $LiClO_4$ where x=10, 20, 30, 40 wt% from now on designated as PPSE1, PPSE2, PPSE3, PPSE4 respectively. The above chemical substance was dissolved in 30ml DMF and stirred at ambient temperature for nearly 24 hours. After a homogeneous solution is formed, the polymer mixture is poured into a petri dish and kept in a vacuum oven at about 70°C. After 48 hours, a dried polymer film was formed.

Results & Discussion

XRD

It can be seen from Figure 1 that all electrolyte membranes have a broad peak at low diffraction angles, indicating that there is an amorphous nature in all polymer systems [27] and have good miscibility among the constituent materials. The amorphous nature of this plasticized blend polymer solid electrolyte system reveals that the lithium salt is not crystallized in the film, rather dispersed at a molecular level within the polymers in the presence of PC. The amorphous nature of the solid electrolyte increases with the increase of PC, resulting in segmented flexible movement, which is essential for enhancing the ionic conductivity in the PPSE's [18, 19].

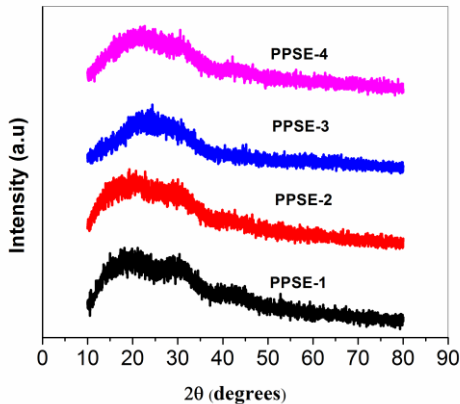


Figure 1 X-Ray Diffraction pattern of plasticized blend polymer solid electrolyte system: (1-x) PMMA : x PC : 10 wt% PVP: 5 wt% $LiClO_4$.

DSC thermo-grams & D.C Ionic conductivity studies

Figure 2 depicts the DSC Thermographs of plasticized blend solid polymer electrolytes and shows the value of T_g . T_g is related to the polymer's segmental flexibility and the solid electrolyte's disordered structure and plays a major role in the case of dc ionic conductivity [9, 10]. T_g value decreases with an increase in PC, and the minimum value has been observed as 402 K for the PPSE2. $\log(\sigma T)$ vs. $10^3/T$ for (1-x) PMMA : x PC : 10 wt% PVP: 5 wt% $LiClO_4$ solid electrolytes is shown in figure 3. In these polymer compositions, the ionic conductivity increases significantly with temperature and the wt% of PC. The maximum enhancement of ionic conductivity can be observed for PPSE2 attributed to the segmental polymer flexibility, which helps in the movement of Li^+ ion in the polymer matrix [10, 19]. The decrease in ionic conductivity of PPSE3 can be understood as an increase in T_g , which causes ions to move slowly in the polymer network.

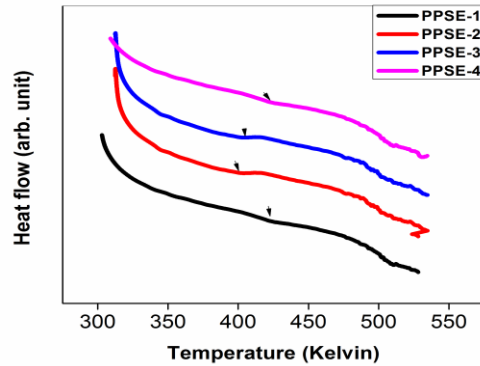


Figure 2: DSC Thermographs of plasticized blend solid polymer electrolytes: (1-x) PMMA : x PC : 10 wt% PVP: 5 wt% $LiClO_4$

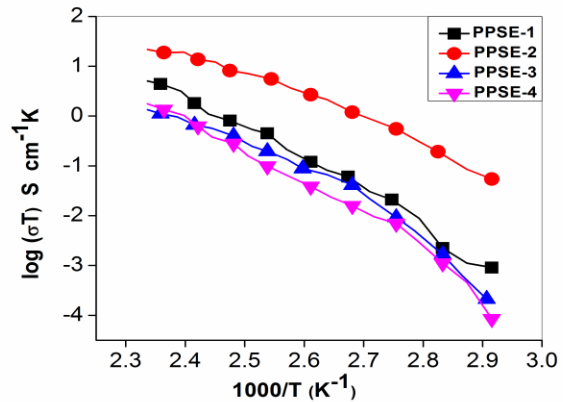


Figure 3: $\log(\sigma T)$ vs. $10^3/T$ for (1-x) PMMA : x PC : 10 wt% PVP: 5 wt% $LiClO_4$ solid electrolytes

Activation energies have been calculated for all these polymer systems using a linear fit program. Activation energy E_a is low as 0.39eV for the sample, which shows high ionic conductivity, indicating that there are less resistive polymer chains with an increase in flexibility favoring the formation of conducting paths for ion transport[20].

Dielectric studies

It can be observed from Figure 4 and Figure 5 that ϵ' and ϵ'' are more distinguished at low frequencies and independent at high frequencies. At low frequencies, the values ϵ' and ϵ'' are high, which may be due to dipole and space charge polarization. At moderate frequencies, the values of ϵ' and ϵ'' start decreasing and reaches almost a zero value at high frequencies, which reveals the absence of space charge polarization and relaxation of dipoles. The higher values of ϵ' and ϵ'' at low frequencies further increase with temperature, which could be due to the enhanced localized charge carrier concentrations [12, 13].

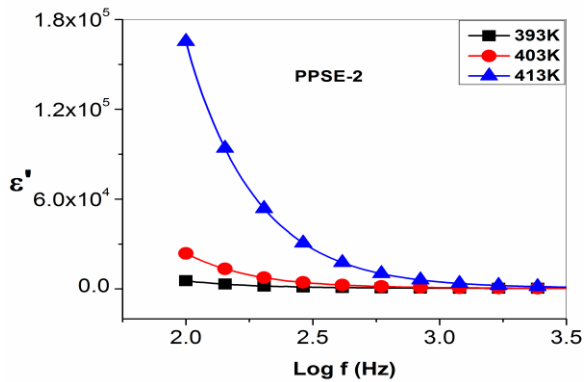


Figure 4: Real part of Dielectric Constant spectrum at different temperatures.

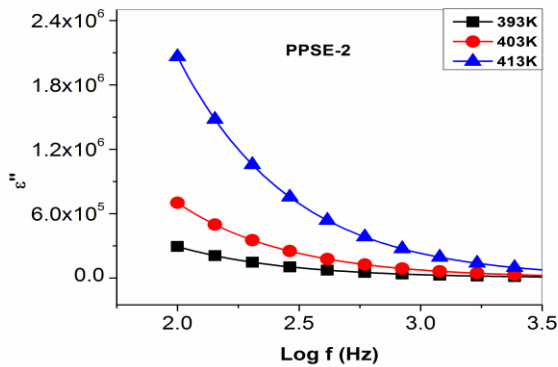


Figure 5: Imaginary Part Dielectric Constant spectrum at different temperatures

Dielectric loss

The value of $\tan\delta$ can be calculated by using the formula $\tan\delta = \epsilon'' / \epsilon'$

where ϵ' and ϵ'' are the real and imaginary parts of dielectric constant.

Figure 6 depicts the variation of $\tan\delta$ with frequency at 393K, 403K, and 413K temperatures for PPSE-2. It has been noticed from the figure that the peaks corresponding to $\tan\delta$ for different temperatures are distinct from one another at lower frequencies and shift towards higher frequencies as the temperature increases. This can be understood that the polymer chain's flexibility exists due to PC's addition such that the Li^+ ion mobility could be increased, resulting in a higher value of dielectric loss [26].

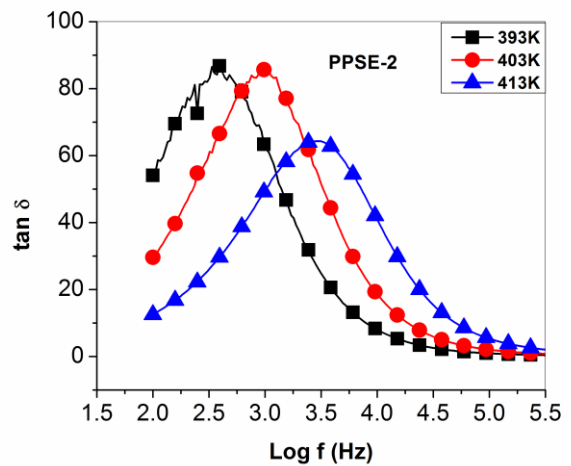


Figure 6: $\tan\delta$ vs. $\log f$ at different temperatures

Conclusions

XRD peaks for (1-x) PMMA: x PC : 10 wt% PVP: 5 wt% LiClO_4 (where $x = 10, 20, 30, 40$ wt%) polymer matrix proved that these solid electrolytes are amorphous in nature. Tg values have been observed from the DSC thermographs. A decrease in Tg values with PC results in the segmental polymer flexibility and favors to increase ionic conductivity. Minimum Tg value is noticed for which maximum highest DC ionic conductivity has occurred in the threshold ratio 70Wt% PMMA: 20Wt% PC: 10Wt% PVP: 5Wt% LiClO_4 . Large values of $\tan\delta$ and shift in the position of the peaks have been noticed, which could be due to the combined effect of polymer segmental flexibility with Li^+ ion. Dielectric studies also have been made for this polymer matrix and studied the lag of dipoles behind the applied field.

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References

- [1] Gao, R; Nam, H.O.; Ko, W.I.; Jang, H, Energies (a) 10(2017), (CrossRef.)
- [2] Kermani, G.Sahraei,E., Energies 10(2017), (Cross Ref.)
- [3] Shazia Farheen, R.D.Mathod, International Journal of Innovative Research in Science, Engineering and Technology, 3(2014), 17523-17527.
- [4] Ye Sol Lim, Hyun-Ah Jung and Haejin Hwang, MDPI Energies, 11(2018), 1-10.
- [5] S Rajendran and T Uma, Bull. Mater Sci., 23(2000), 27-29.
- [6] Poonam Sharma, D.K.Kanchan, Nirali Gondaliya, Springer, Ionics 19(2013),777-785.
- [7] K.Naveen Kumar, Misook Kang, K.Sivaiah, M.Ravi, Y.C.Ratnakaram, Springer, Ionics, 22(2016), 815-825.
- [8] Poonam Sharma, D.K.Kanchan, Nirali Gondaliya, Meenakshi pant, Manish S. Jayswal, Springer, Ionics, 19(2013), 301-307.
- [9] S.Das and A.Ghosh, AIP Advances, 5(2015), 1-9.
- [10] H.M.J.C.Pitwala, M.A.K.L.Dissanayake, V.A.Seneviratne, B.E.Mellander, I.Albinson, Springer, J Solid State Electrochem, 12(2008), 783-789.
- [11] Susan K. Fullerton-Shirey and Janna K. Maranas, American Chemical Society, J. Phys. Chem, C 114(2010), 9196-9206.
- [12] J.Gurusiddappa, W. Madhuri, R. Padma Suvarna, K.Priya Dasan, Indian Journal of Advances in Chemical Science, 4(2016), 14-19.
- [13] Abdelhameed Ahmed EIBellihi, Wafaa Abdallah Bayoumy Masoud and Mahmoud Ahmed Mousa, Bull Korean Chem. Soc., 33(2012), 2949-2954.
- [14] Mohd Raffie Johan, Oon Hooi Shy, Suriani Ibrahim, Siti Mariah Mohd Yassin, Tay Yin Hui, Elsevier, Solid State Ionics 196 (2011) 41-47.
- [15] M.Y.A.Rahman, A.Ahmad, T.K.Lee, Y.Farina, H.M.Dhlan, Scientific Research, Materials Sciences and Application, 2(2011), 818-826.
- [16] Sangamithra Chintapalli and Roger Feech, American Chemical Society, Macromolecules 29(1996), 3499-3506.
- [17] Hslen-Wei Chen, Tzu-Pin Lin, Fing-Chih Chang, Elsevier, Polymer 43(2002) 5281-5888.
- [18] P.Chandra Sekhar, P.Naveen Kumar, A.K.Sarma, International Journal of Scientific & Research Publications, 2(2012), 498-502.
- [19] Chithra M. Mathew, K. Kesavam & S. Rajendran, Hindawi Publishing Corporation, International Journal of Electrochemistry, (2015), 7 pages.
- [20] Chung-Wen Kuo, Wen-Bin Ki, Pin-Rong Chen, Jian-Wei Liao, Ching-Guey Tseng, Tzi-Yi Wu, J.Electrochem.Sci, Int. 8(2013) 5007-5021.
- [21] Y Govinda Reddy, AM. Awasthi, A.Sadananda Chary & S.Narender Reddy, Emergent Materials,1(2018), 175-184.
- [22] Gh. Mohammed, Adel M.El sayed, S. El. Gamal, Journal of inorganic & organometallic polymers & materials, springer science + business media, Lc part of springer nature, 2019, 14pages.
- [23] Nor Hazlizaaini Basri & N.S.Mohammed, Solid State Science & Technology, 17(2009), 63-72.
- [24] Tan Kia, Thesis, University Tunku Abdul Rahman, Master of Engineering Science, (2013), 116-126.
- [25] Manasvi Dixit, Vishal Mathur, Sandhya Gupta, Mahesh Baboo, Kananbala Sharma & N.S.Saxena, Taylor &Francis, Phase Transitions A Multinational Journal, 82(2009), 866-878.
- [26] S. Jayanthi, B. Sundaresan, Ionics, 21(2015),705-717.
- [27] B.Bhanu Prasad and MDVSRilalitha, SSRG International Journal of Material Science & Engineering (SSRG-IJMSE), 6(1)(2020), 5-10.