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Study on new lithium ion conducting electrolyte based on Polyethylene glycol – p-tertoctyl phenyl ether and Lithium Perchlorate

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Abstract: A series of various compositions of Polyethylene glycol-p-pert octyl phenyl ether (Triton) and lithium perchlorate (LiClO_4) polymer electrolytes was prepared. A thorough impedance study was carried out in the frequency range 100 mHz – 7 MHz over the temperature range 303-333K by using biologic model SP-300 electrochemical work station. The highest ionic conductivity of $4.118 \times 10^{-4} \text{ S cm}^{-1}$ was calculated for the composition of 85 wt % triton and 15 wt % LiClO_4 at ambient temperature. The complexation between Triton and LiClO_4 is confirmed by Fourier transform infrared spectroscopy studies. Optical properties of electrolytes were also studied using UV-Visible spectrometer.

Keywords : Triton X-100, Lithium perchlorate, Impedance spectroscopy, Dielectric, FTIR.

1.Introduction :

Rechargeable Li ion cells are the key components of the portable, entertainment, computing and telecommunication equipment required by today's information rich, mobile society[1]. The use of non aqueous electrolytes for batteries and electrochemical capacitors are, in principle, preferred since higher operating voltages can be utilized due to the larger decomposition limits of such electrolyte solutions. Polyethylene glycol – p-tertoctyl phenyl ether is commercially called as Triton X-100. It is liquid, water soluble, non ionic surfactant. It is an octyl phenol ethoxylate consisting of 9 to 10 mole of ethylene oxide and is supplied as a 100 percent active product. Because of its good surface activity, it can be used as surface modifier in the preparation of quantum dots[2] and nano particles[3]. Emulsion polymers formed in the presence of this surfactant have particles of satisfactorily low diameter and exhibit outstanding stability to electrolytes, free-thaw cycling and mechanical stress.

Lithium perchlorate (LiClO_4) is comprised of a small sized cation and a large sized anion. The ionic conductivity is affected by the diffusion rate of ions which depends on the size of the ion. LiClO_4 is more favorable compared to other lithium salts due to the low interfacial resistance when lithium metal was used as anode[4, 5]. Moreover, LiClO_4 has high dissociation energy, thus it is readily soluble in most organic solvents and LiClO_4 is directly soluble in Triton is an additional advantage. Hence, LiClO_4 is chosen as ionic salt. In the present work, a new attempt is made by using a surfactant, Triton, as polymer host to prepare polymer electrolyte and to study its ionic conductivity.

2. Experimental :

Polyethylene glycol – p-tertoctyl phenyl ether solution obtained from Himedia with >98% purity, Lithium perchlorate from Himedia with >99% were used without further purification. Lithium perchlorate is added into polyethylene glycol – p-tertoctyl phenyl ether solution and the solution was stirred overnight to ensure complete dissolution of the polymer–salt. Polyethylene glycol – p-tertoctyl phenyl ether-LiClO₄ electrolytes were prepared in the compositions of 100:0, 95:05, 90:10 and 85:15 wt %. Then they were characterized by FTIR, Impedance and UV visible studies. FTIR spectra of electrolyte solutions were recorded in the range of 400-4000 cm⁻¹ using JASCO FT/IR – 4100 spectrometer. Conductivity data of electrolyte solutions wererecorded using Biologic SP-300 electrochemical workstation. Two platinum electrodes with fixed distance were used as blocking electrodes. Optical property of electrolytes was analyzed in the range 200-800 nm using UV -2600 UV-Vis spectrometer SHIMADZU.

3. Results and Discussions :

3.1. FTIR studies :

FTIR spectra of pure Triton, pure LiClO₄ and its complexes are shown in Figure 1. The spectrum of pure Polyethylene glycol – p-tertoctyl phenyl ether (Fig 1.a) agrees well with the literature [2] on its characteristic modes appearing at wave numbers 3478cm⁻¹, 2950cm⁻¹, 2858cm⁻¹, 1609cm⁻¹, 1510cm⁻¹, 1244 cm⁻¹and 1103 cm⁻¹.

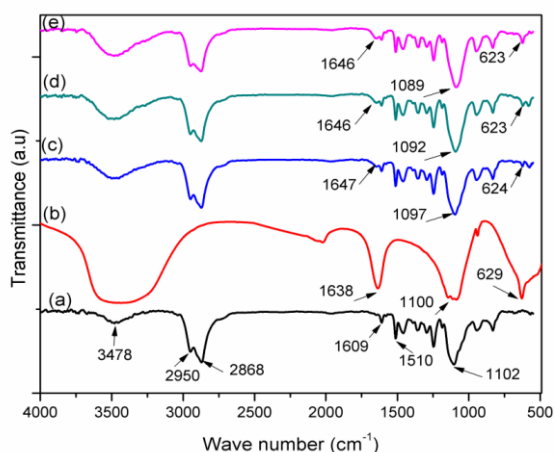


Figure 1. FTIR spectrum of (a) Pure Triton, (b) LiClO₄ (c) 5 wt % (d) 10 wt % (e) 15 wt % LiClO₄ added electrolytes

The broad peak around 3478 cm⁻¹ is ascribed to –OH group of Triton. The sharp peaks at 2950 and 2868 cm⁻¹ are attributed to asymmetric CH₂ stretching and symmetric CH₂ stretching respectively. The peaks at 1609 cm⁻¹ and 1510 cm⁻¹ are assigned to stretching vibration of benzenoid group. The peak which appeared at wave number 1103 cm⁻¹ is associated with stretching vibration aromatic ether group. When LiClO₄ is added to the polymer, the ether oxygen vibrational group appeared at 1102 cm⁻¹ get shifted to 1097 cm⁻¹, 1092 cm⁻¹, 1089 cm⁻¹ for 5, 10, 15 wt % LiClO₄ added electrolyte solutions (fig 1.c-e) respectively with increasing in intensity which are attributed to interaction of asymmetrical stretching vibration of ClO₄⁻ ion appeared at 1100 cm⁻¹ (fig 1.b). The peak appeared at 1638 cm⁻¹ in pure LiClO₄ (fig 1.b) is due to the stretching vibration of pure LiClO₄[5] that is shifted to 1647cm⁻¹, 1646cm⁻¹ and 1646 cm⁻¹ in 5, 10 and 15 wt % LiClO₄ added electrolyte solutions respectively with decrease in intensity. The peak at 629 cm⁻¹ (fig 1.b) which is attributed to coordinated ClO₄⁻ ion vibration[6] is shifted to 624 cm⁻¹, 623 cm⁻¹, 623 cm⁻¹ for 5, 10, 15 wt % LiClO₄ added electrolyte solutions (fig 1.c-e) respectively with increasing in intensity. The shifts confirm the interaction of ether oxygen group of polymer with dissociated LiClO₄. It reveals the polymer-salt complex formation.

3.2. AC impedance studies :

Impedance spectroscopy provides a better understanding in the conduction mechanism and mobility processes [7]. In order to calculate the ionic conductivity of electrolyte solutions, the following relationship is used:

$$= (t / R_b A)$$

Where σ is the conductivity in Siemens per centimeter, t is the distance between two platinum electrodes in centimeter, R_b is the bulk resistance in Ω obtained from the Nyquist plot, and A is the surface area of the platinum blocking electrodes in square centimeter. Figure 2 (a-d) shows the Nyquist plot of pure Triton and its complexes with different (5, 10, 15 wt %) amounts of LiClO_4 .

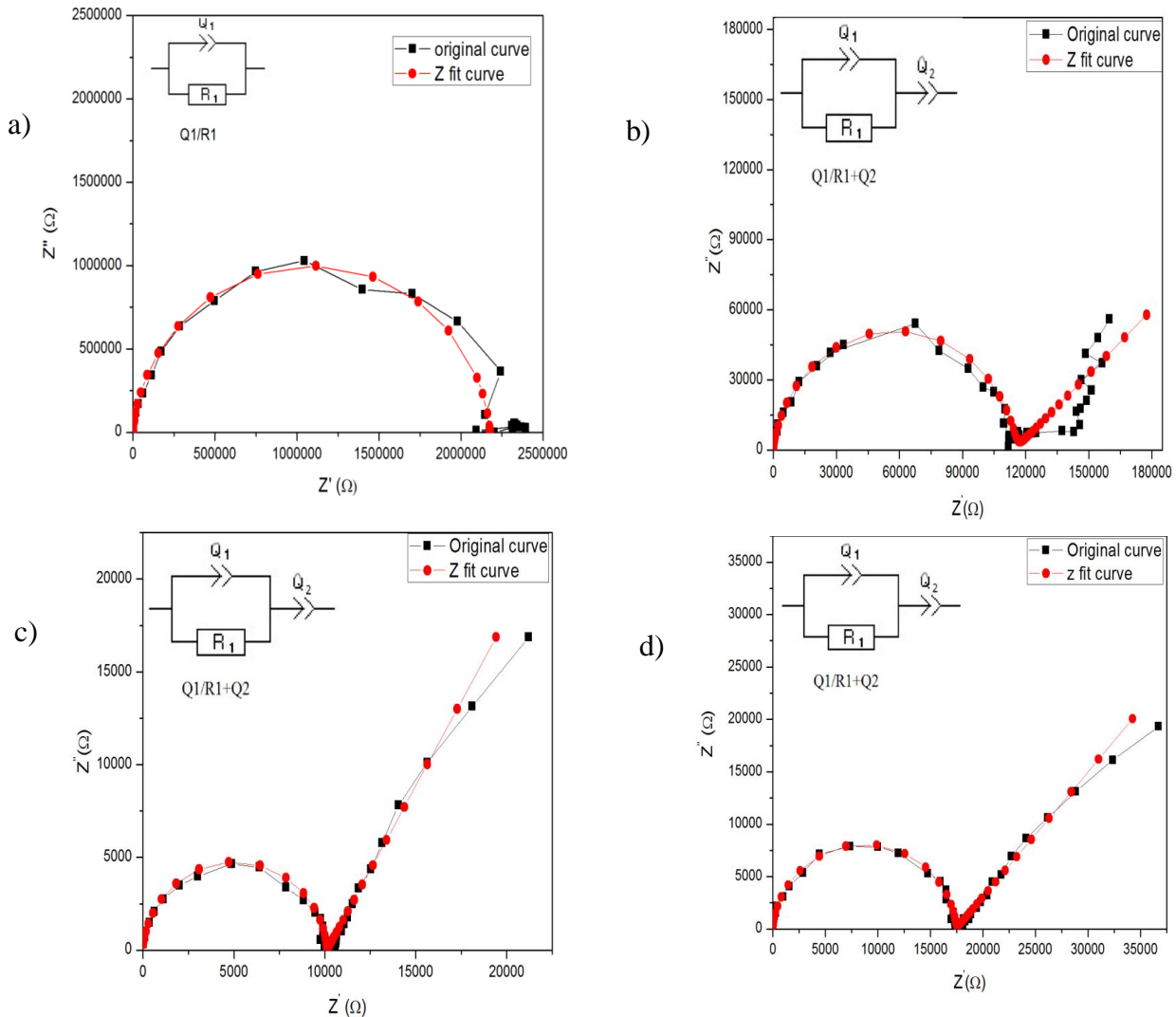


Figure 2 Nyquist plot of Triton with various amounts (a) 0 wt % (b) 5 wt % (c) 10 wt % (d) 15 wt % of LiClO_4

From the figure 2a, a semi circle alone is observed for pure triton and it does not show any spike in low frequency region which is caused by polarization of ions at the electrode electrolyte interface. On the addition of various concentration of LiClO_4 to the polymer (figure 2. b-d), a semi circle along with inclined straight lines obtained. The spike should appear as a straight line which is parallel to the imaginary axis but the inhomogeneity on the surface of the blocking electrode causes the curvature.

When salt concentration increases, bulk resistance decreases and hence the conductivity increases. The increase of conductivity is due to the enhancement of charge carrier concentration owing to the dissociation of LiClO_4 into Li^+ and ClO_4^- ions that exist as solvated ions in the polymer electrolytes. Bulk resistance is calculated by fitting complex impedance plot using Z FIT software. The fitting curves for all electrolytes are also shown in figure 2. Equivalent circuit of each impedance plot is given as insert figure 2 respectively. Conductivity values of prepared electrolytes are given in table 1.

Table 1 Ionic conductivity and activation energy for various composition of Triton–LiClO₄

S.No	Sample designation	Composition of Triton-LiClO ₄ Wt %	Ionic conductivity (S cm ⁻¹) at 303 K	Activation energy (eV)	β value
1	T100	100:0	1.913 x 10 ⁻⁶	0.5021	0.6913
2	T95	95:05	3.626 x 10 ⁻⁵	0.4662	0.5325
3	T90	90:10	2.388 x 10 ⁻⁴	0.4601	0.7362
4	T85	85:15	4.118 x 10 ⁻⁴	0.4523	0.7624

polymer electrolyte

3.3 Temperature dependent conductivity:

Figure 3 shows the Arrhenius plot of pure polymer and polymer electrolyte solutions. It can be observed that, as the temperature increases, the conductivity of pure polymer and 5, 10 and 15 wt % of LiClO₄ added electrolytes also increases which is due to the enhancement of ionic mobility [5,8].

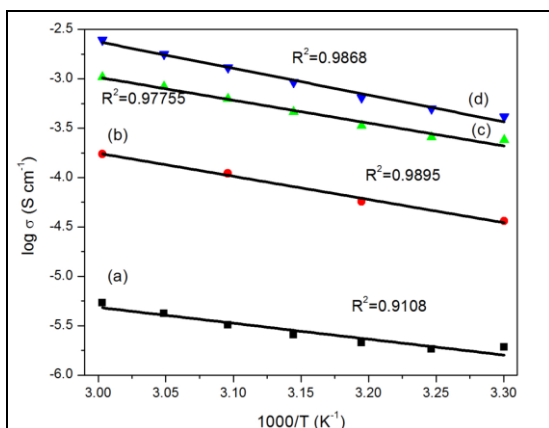


Figure 3.Temperature-dependence of ionic conductivity of (a) T100 (b) T95 (c) T90 (d) T85 electrolyte solutions

Activation energy (E_a) was calculated using the slope obtained by linear fitting the curves from $\log \sigma$ versus $1000/T$ graph which is based on Arrhenius rule $\sigma = \sigma_0 \exp[-E_a/(KT)]$ where, σ_0 is the pre-exponential factor, K is the Boltzmann constant, T is absolute temperature and E_a is the activation energy. Regression value of linear fit is about 0.98-0.99 for electrolytes and greater than 0.91 for pure polymer indicates that appreciable linearity is maintained. The linear fit confirms that the polymer electrolyte system obeys Arrhenius equation. Table 1 lists E_a of all the prepared electrolytes. The value of E_a is low for highest conducting electrolyte solution. It indicates that the energy which require for hopping can be reduced with increasing the salt concentration.

3.4 Dielectric relaxation studies:

Dielectric relaxation studies are a vital tool to show the relaxation of dipole in polymer electrolyte. The real (ϵ') and imaginary part (ϵ'') of dielectric permittivity spectra are shown in figure 4.

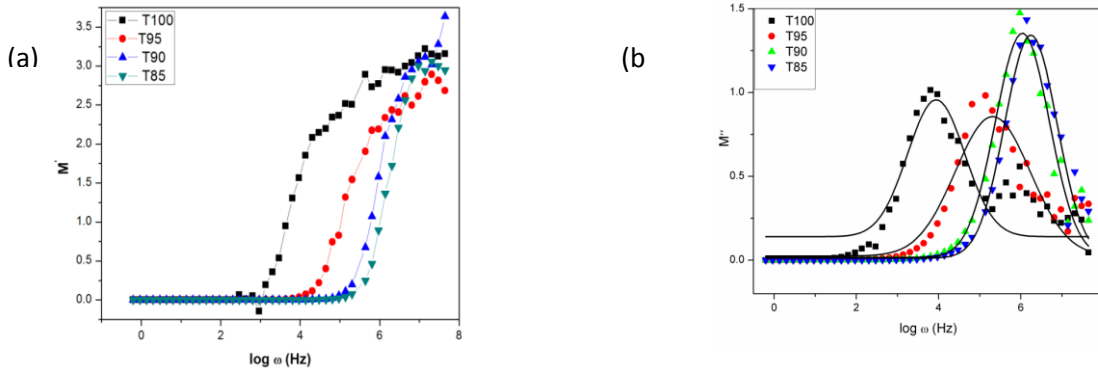


Figure 4 variation of dielectric permittivity (a) real part (b) imaginary part with frequency.

The plot demonstrates that the dielectric constant is high at low frequencies and gradually decreases and approaches zero at high frequency. The low frequency dispersion region corresponds to the contribution of charge accumulation at the electrode - electrolyte interface. At high frequencies the periodic reversal of electric field occurs so fast, there is no excess ion diffusion in the direction of the field[9,10]. The highest value of ϵ' for T85 is due to the greater number of charge carrier at space charge accumulation region, resulting in a rise in the equivalent capacitance[11]

3.5 Dielectric modulus studies:

The dielectric modulus is relying on the formulation of a dielectric modulus, which has been used to understand the conductivity relaxation. Figure 5 shows the real (M') and imaginary (M'') modulus formalism.

It is observed from the plots that M' and M'' are very low at low frequencies which are due to the electrode polarization phenomenon which makes a negligible contribution. The peaks in the M'' modulus formalism at high frequencies show that the polymer electrolyte solutions are ionic conductors [9, 10]. It is also observed that the peaks of M'' are shifted towards higher frequency side upon the addition of LiClO_4 . By fitting the peaks using Gaussian distribution, the coefficient β values of electrolytes are calculated and the values are given in the table 1.

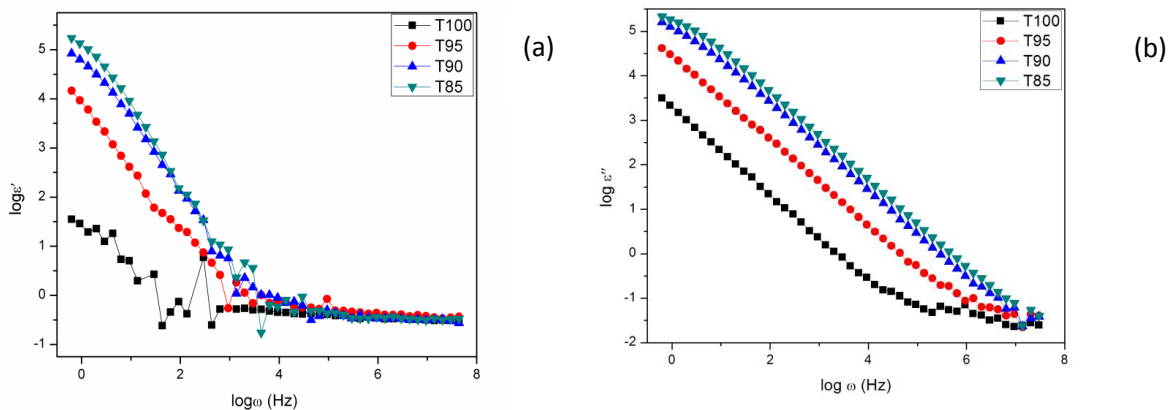


Figure 5 Variation of dielectric modulus (a) real part (b) imaginary part with frequency

3.6 UV Visible studies:

Influence of LiClO_4 concentration on the transmittance property of polymer host is analyzed by UV Visible spectroscopy. The UV visible spectrum of Triton and its complexes with (0, 5, 10, 15 wt %) LiClO_4 is shown in Figure 6.

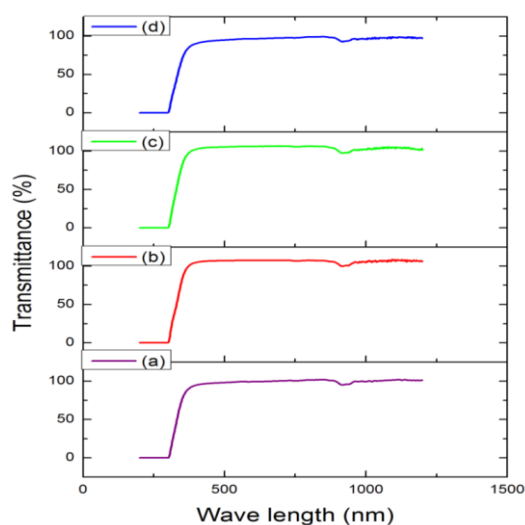


Figure 6 UV visible spectra of Triton with various amounts (a) 0 wt % (b) 5 wt % (c) 10 wt % (d) 15 wt % of LiClO₄

All the electrolyte samples have sharp cut off wave length at 296 nm in which transmittance value of electrolytes comes to 0% from maximum. Hence, these pure triton and electrolyte solutions can be used as a filter for ultraviolet region. It is also observed that the salt concentration does not affect the cut off wave length and thus optical property of electrolytes.

4. Conclusions :

A series of Triton X-100 - LiClO₄ based electrolytes are prepared by varying the LiClO₄ concentration. Complex formation between Triton and LiClO₄ is confirmed by FTIR spectroscopy. It is found that the conductivity increases with increasing the salt concentration which is due to the increment of number of charge carriers. Maximum ionic conductivity of $4.118 \times 10^{-4} \text{ S cm}^{-1}$ is achieved for sample containing 15 wt % of LiClO₄. The low activation energy of 0.45 eV is also observed for the same electrolyte. Dielectric behavior is analyzed using dielectric constant (ϵ' and ϵ'' dielectric moduli (M' and M'') of the samples. Optical property of the electrolyte solutions is not affected upon addition of salt.

References :

1. Tarascon J. H, Armand M, Issues and challenges facing rechargeable lithium batteries Nature 414 (15) 2001.
2. Lin Yang, Jianguo Zhu, Dingquan Xiao, Microemulsion-mediated hydrothermal synthesis of ZnSe and Fe doped ZnSe quantum dots with different luminescence characteristics RSC Advances 2012 (2) 8179-8188.
3. Al-Omai N. A, Reda, S. M, Al-Hajri F. M, Triton Facilitated spherical TiO₂ Nanoparticles and Their Advantage in a Dye-Sensitized Solar Cell Advances in Materials Physics and Chemistry, 2014, 4, 29-32.
4. P. Liu, L. Yu, H. Liu, L. Chen, L. Li, Glass transition temperature of starch studied by a high-speed DSC Carbohydr. Polym. 77 (2009) 250–253.
5. K.H. Teoh, Chin-Shen Lim, S. Ramesh, Lithium ion conduction in cornstarch based solid polymer electrolytes, Measurement 48 (2014) 87–95.
6. Kulasekarapandian, K, Jayanthi, S, Muthukumari, A, Arulsankar, A, Sundaresan, B, Preparation and Characterization of PVC – PEO Based Polymer Blend Electrolytes Complexed With Lithium Perchlorate International Journal of Engineering Research and Development 5 (13) 2013.
7. K. H. Teoh, S. Ramesh, A. K. Arof, Investigation on the effect of nano silica towards Corn starch-lithium perchlorate based polymer electrolytes, J Solid State Electrochem (2012) 16:3165–3170.
8. Liew C.W, Ramesh S, Ramesh K, Arof A.K, J solid state Electrochem, 16 (2012) 1869-1875.
9. Ramesh S, OwgPoh Ling, Effect of ethylene carbonate on the ionic conduction in poly (vinylidene fluoride-hexafluoropyrene) based solid polymer electrolytes, Poly.chem 1 (2010) 702-707.

10. Ramesh S, Chai M.F, Conductivity, dielectric behavior and FTIR studies of high molecular weight poly (vinyl chloride)-lithumtriflate polymer electrolytes, Mater.Sci. Eng B 139 (2007) 240-245.
11. Poli A.R, Kumar R, Ionic conductivity and electrochemical studies on Mg²⁺ - ion conducting PEG Al₂O₃ composite polymer electrolytes, E.J Chem 1 (2011) 347-353.
