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Conductivity and dielectric behaviour of organic binary solution of Lithium Nonafluoro-1-butanefluorobutanesulfonate as electrolytes for Lithium ion batteries

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Abstract : Liquid electrolytes of 0.1M Lithium Nonafluoro-1-butanefluorobutanesulfonate were prepared using PC and DME solvent with different volume ratio of 1v%:1v%, 1v%:2v% and 2v%:1v%. The effect of volume ratio of solvent on the ionic conductivity and dielectric behaviour of the electrolyte was measured. The maximum conductivity, measured from AC Impedance Spectroscopy was found to be 2.52 mScm^{-1} for 1v%:1v% of PC, DME. The dielectric behaviour was analysed using dielectric permittivity (ϵ'), Modulus (M') and dissipation factor ($\tan\delta$). The ionic transference number was estimated by chronoamperometry, using platinum blocking electrodes and was found as 0.99 for all the liquid electrolytes.

Introduction

Commercialized liquid electrolytes for lithium ion batteries are prepared by dissolving lithium salt in organic solvents such as PC, EC, DEC, DMC, MEC, DME etc[1-3]. The properties of the liquid electrolytes mainly depend on dielectric constant and viscosity of the solvents. The high dielectric of the solvent helps to dissociate the salt while low viscosity promotes the motion of ions in the solution. But, it is difficult to find such solvents which possess high dielectric constant and low viscosity. Hence, mixed solvents are used for the preparation of liquid electrolytes. Here, Propylene carbonate and 1,2-Dimethoxyethane have been used as binary organic solvent. Cyclic carbonate, PC has been used as the high polarity solvent for primary lithium ion batteries. Linear carbonate of 1,2-Dimethoxyethane has low melting point, low viscosity and much lower dielectric constant (7.58) than PC (66.1). The blending of a high-polarity solvent and a low viscosity solvent produce synergistic effect on conductivity [4]. Solvent diffusion and ion conduction of PC-DEC and PC-DME binary solvent electrolytes of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ have been studied[5]. Molar volumes, viscosities and activation free energies of LiClO_4 and LiBr in the mixed solvents of PC with DME were investigated for understanding the solute-solvent interaction of the system[6]. The present work aims to study the effect of ratio of binary solvent on the conductivity and dielectric properties of liquid electrolytes.

Experimental

Lithium nonafluoro-1-butanefluorobutanesulfonate salt was purchased from TCI (Purity >95%). The solvents of anhydrous propylene carbonate (Purity 99.7%) and 1,2-Dimethoxyethane (Purity 99.5%) was purchased from sigma Aldrich. Three different liquid electrolytes were prepared by varying the PC and DME ratio such as

1v%:1v%, 1v%:2v% and 2v%:1v% with constant salt concentration of 0.1M for all solvent ratio. All the preparations were carried out inside the glove box (MIKROUNA). Moisture and oxygen levels in the glove box were maintained less than 0.1ppm.

The ionic conductivity of the samples was calculated from the measurement of electrochemical impedance data that were obtained by using Biologic SP300 Electrochemical workstation. The above study was performed by using platinum blocking electrodes over a frequency range of 1Hz to 7MHz at room temperature.

Results and discussion

The ac impedance analysis

Fig.1 shows the complex impedance diagram of 0.1M salt concentration of liquid electrolytes for different solvent ratio of PC and DME such as 1v%:1v%, 1v%:2v% and 2v%:1v%. The ionic conductivity of the liquid electrolytes at room temperature has been calculated using the following formula and the conductivity values are mentioned in the Table.1.

$$\sigma = \frac{d}{AR_b} \dots \dots \dots (1)$$

Where d and A are thickness and area of an electrolyte respectively. The R_b is bulk resistance of an electrolyte that is evaluated from an impedance plot. The fitting on the complex impedance plot by using Z Fit in Biologic EC-Lab (V 10.36) software, yields the bulk resistance (R_b). The plot shows that semicircle is appeared at high frequency region followed by a spike shows an inclined straight line parallel to imaginary axis at low frequency region, but double layer at the inhomogeneous electrode and electrolyte interface causes the curvature [7]. The semicircle formed owing to parallel combination of resistor and capacitor in the electrolyte. From the plot, it is observed that the maximum conductivity of 2.52 mScm^{-1} has been obtained for 1v%:1v% (PC:DME) than other ratio of solvents. Based on the above discussion, it is understood that in 1v%:2v% ratio of PC:DME, the dielectric constant value is reduced by increasing the amount of DME. Hence, net ions dissociation is reduced. Meanwhile, in the case of 2v%:1v% ratio of PC:DME, the mobility of ions is decreased due to high viscous nature of PC compared to DME [8].

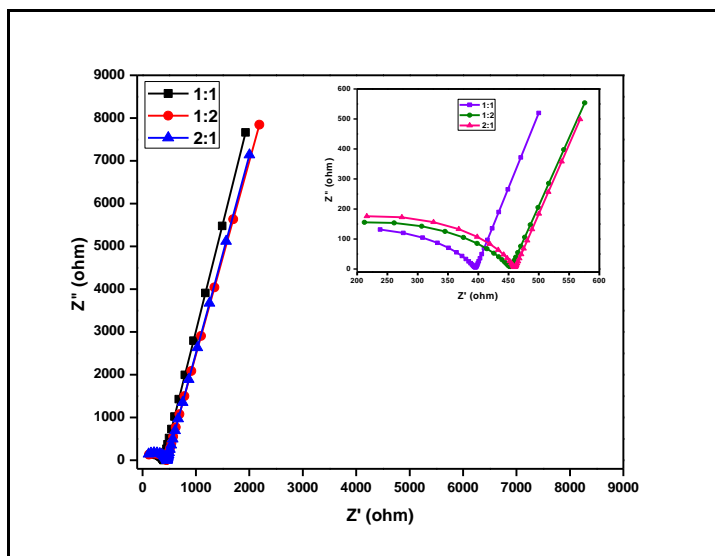


Fig.1. Complex impedance spectra of liquid electrolytes for all solvent ratio (PC:DME) at room temperature.

Conductivity – frequency dependence studies

The logarithmic plots of the conductivity as a function of frequency for all samples at room temperature are depicted in Fig.2. The frequency dependent conductivity is demonstrated well by Jonscher's power law. The σ_{dc} values of these electrolytes are determined by fitting the high frequency σ values to the Jonscher power law $\sigma(\omega) = \sigma_{dc} + A\omega^n$ where A is the pre-exponential factor and n is the fractional exponent ranging between 0 and 1. The evaluated values of σ_{dc} are given in the Table.1. A significant decrease in σ values start with decrease in

frequency below, which is due to the involvement of electric double layer capacitive effect and this effect dominated further shift towards lower frequency range. In the high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency.

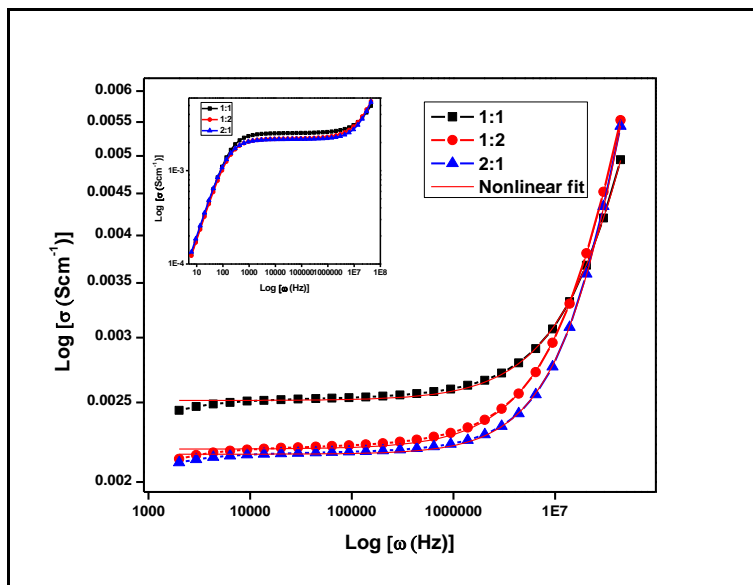


Fig.2. ac conductance spectra of liquid electrolytes for all solvent ratio (PC:DME).

Dielectric relaxation studies

The variation of real (ϵ') and imaginary (ϵ'') parts of complex dielectric constant as a function of frequency for various solvent ratio are shown in Fig.3.a and 3.b respectively. All the electrolytes exhibited the same kind of behaviour. Both ϵ' and ϵ'' rise sharply towards low frequency which is due to electrode polarization effects. At high frequencies, ϵ' maintains a constant value due to high periodic reversal takes place so fast that there is no excess ion diffusion in the direction of the electric field[9]. At low frequency region, a polarization peak in the dielectric loss spectra is appeared due to the accumulation of ionic charges[10]. A high dielectric constant value is observed for 2v%:1v% solvent ratio of PC:DME owing to high polarity nature of PC.

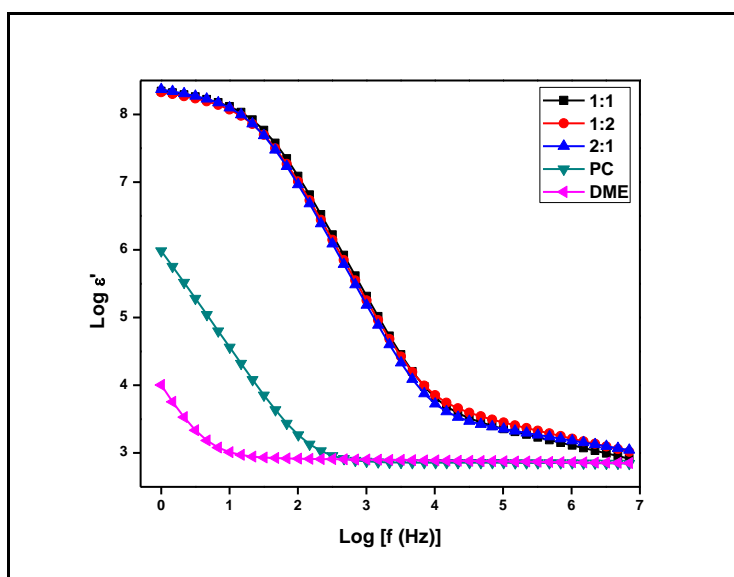


Fig.3.a. Real part of dielectric constant as a function of frequency of liquid electrolytes for all solvent ratio (PC:DME)

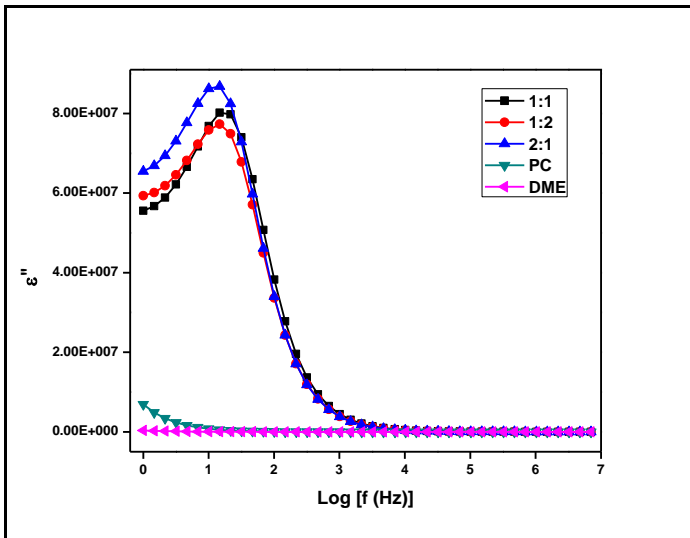


Fig.3.b.Imaginary part of dielectric constant as a function of frequency of liquid electrolytes for all solvent ratio (PC:DME) Loss tangent spectra

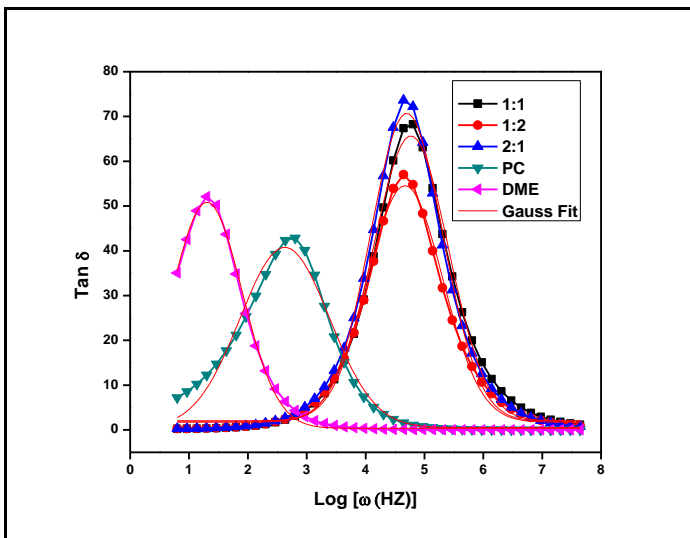


Fig.4.Tanδ as a function of frequency of liquid electrolytes for all solvent ratio (PC:DME)

Fig.4 shows the dielectric spectra in terms of the loss factor $\tan\delta = \epsilon''/\epsilon'$ versus the frequency for three different solvent ratio. The graph is fitted with gaussian fit for further analysis. We noticed clearly that $\tan\delta$ increases with increasing frequency and reaches a maximum. Then it decreases for further increase of frequency. In the spectra, the maximum $\tan\delta$ value has been obtained for 2v%:1v% of PC:DME. This may be due to the high dielectric nature of PC get maximum contribution in this mixture. Meanwhile, in the case of 1v%:2v% of PC:DME, DME is highly dominated and hence low dielectric constant of the mixture[11].From this plot, relaxation time is calculated by using the relation $\tau = 1/\omega$ where ω is the angular frequency of the applied electric field. The calculated τ values for all the prepared liquid electrolytes at room temperature are tabulated in the Table.1. Based on the dissipation factor plot, a low relaxation time is obtained for 1v%:1v% solvent ratio which is consistent with the conductivity analysis which shows higher conductivity [12].

Table.1. Conductivity and Relaxation parameters of liquid electrolytes for all solvent ratio (PC:DME)

Sl.no	Solvent ratio (v%:v%)	R _b value (ohm)	DC Conductivity from EIS (mS/cm)	DC conductivity from Joncher's Power Law (mS/cm)	Relaxation time(sec)
1	1:1	396	2.52	2.51	1.70E-05
2	1:2	453	2.2	2.19	2.14E-05
3	2:1	460	2.17	2.16	2.01E-05

Transport number measurement

The transport number of an electrolyte is an important study to know whether the conductive is due to ions or electrons in liquid electrolytes. The total ionic transference number of liquid electrolytes has been measured from chronoamperometry study. For this study, platinum was used as blocking electrodes. Fig.5 shows the results of dc polarization measurements for all liquid electrolytes. A fixed small DC potential (1 volt) was applied across the blocking electrodes, the current was measured as a function of time, to allow the samples to become fully polarized. The transference number has been calculated using the following relation

$$t_{ion} = \frac{I_i - I_f}{I_i} \dots\dots\dots (2)$$

$$t_{ele} = \frac{I_f}{I_i} \dots\dots\dots (3) \text{Where } I_i \text{ is the initial current and } I_f \text{ is the final residual current.}$$

For all compositions of liquid electrolytes, the values of the ionic transference number (t_{ion}) are in the range of 0.99. This result suggests that, the charge transport in these electrolyte systems is predominantly due to ions, and electronic contribution to the total current is negligible.

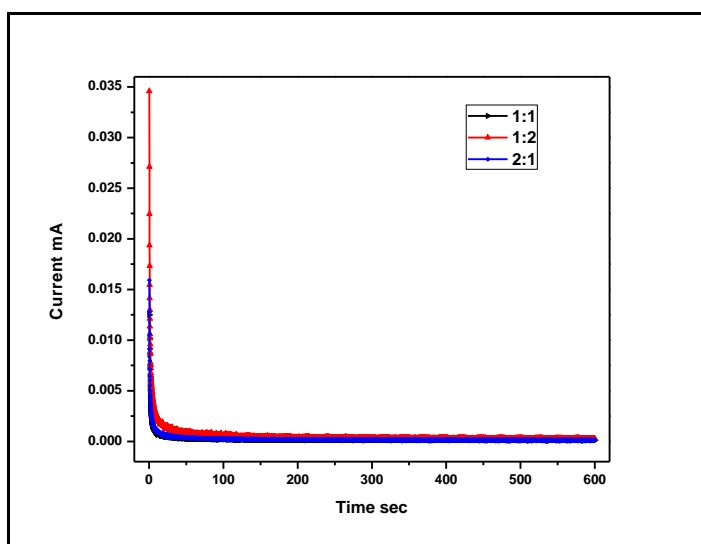


Fig.5. Polarization current versus time curve of liquid electrolytes for all solvent ratio (PC:DME) at room temperature.

Conclusion

The 0.1M salt concentration liquid electrolytes have been prepared with different solvent ratio of PC:DME such as 1v%:1v%, 1v%:2v% and 2v%:1v%. The ionic conductivities of the electrolytes have been measured from ac impedance technique and Jonsher's power law. The maximum conductivity of 2.52 mScm⁻¹ has been obtained for 1v%:1v% solvent ratio of PC, DME. Chronoamperometry study has confirmed that all liquid electrolytes have only ionic movements for conductivity and negligible amount of electrons.

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References

1. L. Yang, A. Xiao, Brett L.Lucht, Investigation of solvation in lithium ion battery electrolytes by NMR spectroscopy *Journal of Molecular Liquids* 154 (2010) 131-133.
2. M. Dahbi, F. Ghamouss, F. Tran-van, D. Lemordant, M.Anouti, Comparative study of EC/DMC LiTFSI and LiPF6 electrolytes for electrochemical storage *Journal of Power Sources* 196 (2011) 9743-9750.

3. K.Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries *Chemical Reviews* 104 (2004) 4303.
4. N. Nanbu, K. Takimoto, M. Takehara, Makotove, Y. Sasaki, Electrochemical properties of fluoropropylene carbonate and its application to lithium-ion batteries *Electrochemistry Communication* 10 (2008) 783-786.
5. K. Hayamizu, Y. Aihara, Ion and solvent diffusion and ion conduction of PC-DEC and PC-DME binary solvent electrolytes of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ *Electrochimica Acta* 49 (2004) 3397-3402.
6. Y. Zhao, J. Wang, Z. Yan, K. Zhuo, Molar volumes and viscosities of LiClO_4 and LiBr in propylene carbonate + 1,2-dimethoxyethane mixed solvents at 298.15K *Fluid Phase Equilibria* 244 (2006) 105-110.
7. J.H. Ambyus, C.T. Moynihan, P.B. Macedo, Conductivity Relaxation in a concentrated Aqueous Electrolyte Solution *The Journal of Physical Chemistry* 76 (1972) 22.
8. M. Ishikawa, S.-Q. Wen and Y. Matsuda, Ionic association of lithium salts in propylene carbonate/1,2-dimethoxyethane mixed systems for lithium batteries *Journal of Power Sources* 45 (1993) 229-236.
9. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, ac impedance, DSC and FT-IR Investigations on (x) PVAc-(1-x) PVdF blends with LiClO_4 *Materials Chemistry and Physics* 98 (2006) 55-61.
10. A. Manuel Stephan, T. Premkumar, N.G. Renganathan, S. Pitchumani, R. Thirunakaran, N. Muniyandi, Ionic conductivity and FT-IR studies on plasticized PVC/PMMA blend polymer electrolytes *Journal of Power Sources* 89 (2000) 80-87.
11. S. Lee, S. S. Park, Thermodynamic and dynamic properties in binary mixtures of propylene carbonate with dimethyl carbonate and ethylene carbonate *Journal of Molecular Liquids* 175 (2012) 97-102.
12. N. Vijaya, S. Selvasekarapandian, G. Hirankumar, S. Karthikeyan, H. Nithya, C.S. Ramya, M. Prabhu, Structural, vibrational, thermal, and conductivity studies on proton-conducting polymer electrolyte based on poly (N-vinylpyrrolidone) *Ionics* 18 (2012) 91-99.
