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Conductivity variation of the liquid electrolyte, EC : PC : LiCF₃SO₃ with salt concentration

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Abstract

It is a well known fact that liquid electrolytes inherit better conductivity values than other electrolytes such as solid electrolytes and polymer electrolytes. Basically, a liquid electrolyte consists of a salt dissolved in a solvent or a mixture of solvents. Their conductivity values therefore depend on the salt concentration as well as solvent concentration. Present study is based on the liquid electrolyte, ethylene carbonate (EC), propylene carbonate (PC) and lithium trifluoromethane sulfonate (LiCF₃SO₃ – LiTF). Its conductivity variation with the salt concentration was investigated using AC impedance spectroscopy. The maximum conductivity observed at room temperature (RT) was $2.80 \times 10^{-3} \text{ S cm}^{-1}$ at the salt concentration of 0.85 mol kg^{-1} . To explore the reasons governing the conductivity below and above that salt concentration, viscosity measurements were done using a Ostwalds viscometer. Up to the salt concentration of 0.85 mol kg^{-1} , conductivity increases. Hence, it can be assumed that due to the increment of charge carrier concentration with salt concentration, conductivity increases up to 0.85 mol kg^{-1} . After that, the effect of viscosity may dominate resulting in conductivity reduction. According to the observations, with the salt concentration, viscosity increased. The carrier mobility and hence, the conductivity decrease with viscosity. Conductivity variation with temperature of all samples followed the Vogel Tamman Fulcher (VTF) behaviour.

1. INTRODUCTION

Liquid electrolytes have been known as better candidates for various applications due to their considerable ionic conductivities. At the onset of introducing batteries, liquid electrolytes had shown good performance. Due to some disadvantages such as leaking and corrosion, attention has been diverted towards solid electrolytes. But, almost all types of solid electrolytes do not possess conductivities well above liquid electrolytes. Hence, liquid electrolytes still dominate in applications. In the present study, we have investigated the variation of conductivity with salt concentration in the

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liquid electrolyte EC, PC and LiCF_3SO_3 . Our objective was to find the factors governing the conductivity variation and to determine the salt concentration that gives the maximum room temperature conductivity.

2. EXPERIMENTAL

A mixture of ethylene carbonate (EC) (ALDRICH), propylene carbonate (PC)(Bie and Berntsen A-S, 99%) of 1:1(by weight) was dried over molecular sieves for 24 hours. The required amount of lithium trifluoromethane sulfonate ($\text{LiCF}_3\text{SO}_3 - \text{LiTF}$) (3M) was mixed in and subsequent purification was done by percolating through activated alumina. All the preparation steps were carried out inside a glove box (Vacuum Atmosphere Corp.) purged with Ar. Nine samples with different salt concentrations were prepared. AC measurements were done in the frequency range 1 Hz to 1 MHz from -20°C to 60°C . The complex impedance data were gathered using a computer controlled Solatron SI 1260 impedance analyzer. For each electrolyte sample, two temperature scans were performed. Data analysis was accomplished with the NLLS (Non Linear Least Square) fitting routine EQUIVCRT developed by Boukamp [1]. To investigate the factors affecting the conductivity, viscosity measurements of the liquid electrolytes were done using the Ostwald's Viscometer.

3. RESULTS AND DISCUSSION

Conductivity variation of the liquid electrolytes at RT with different salt concentrations is shown in Fig. 1.

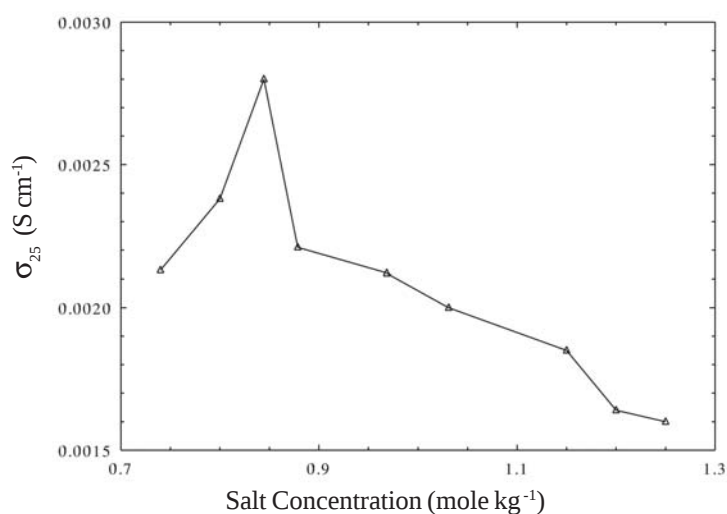


Fig. 1 Room temperature conductivity (σ_{25}) variation of the liquid electrolyte samples with salt concentration.

Room temperature conductivities are comparable with the values reported in literature for similar compositions [2]. The variation follows the trend ; as salt concentration increases, conductivity increases and then reaches a maximum and again reduces. At the salt concentration of 0.85 mol kg^{-1} , the conductivity maximum occurs with a value of $2.80 \times 10^{-3} \text{ S cm}^{-1}$. Appearance of a maximum reflects the interplay of carrier concentration, mobility and ion pairing. To explain this in detail it is worthwhile to refer to the expression,

$$\sigma = ne\mu \quad (1)$$

where σ , n , e and μ stand for conductivity, carrier concentration, electron charge and ion mobility respectively. When the salt concentration increases, the number of available charge carriers increases. As a result, the conductivity increases. At high salt concentrations, charge carriers tend to form ion pairs that are electrically neutral. They might be responsible for conductivity reduction. Apart from this, with increasing salt concentration, viscosity increases. This is clearly evidenced from the results obtained for viscosity measurements shown in Fig. 2.

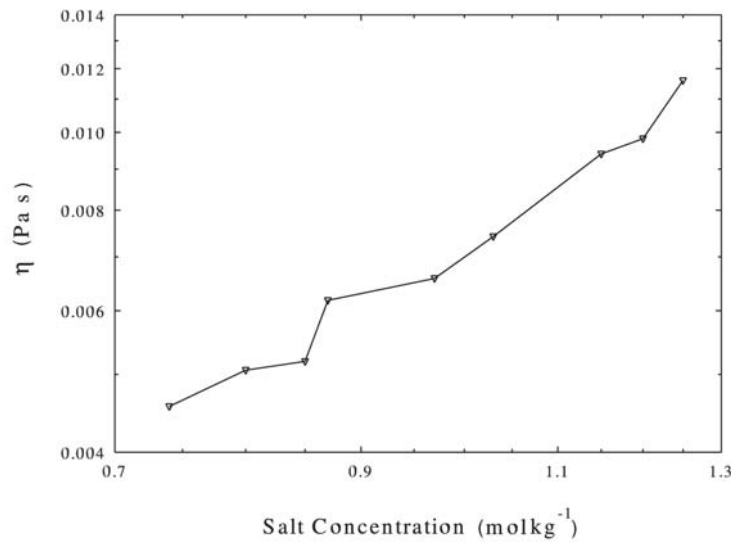


Fig. 2 Viscosity increment of the liquid electrolyte samples at RT with salt concentration.

It is seen that viscosity increases with salt concentration. Upon the increment of viscosity, mobility of the carriers decreases. If the mobility is the only factor governing the conductivity of the electrolytes, conductivity should decrease with increasing salt concentration. But, according to Fig. 1, conductivity increases up to the concentration of 0.85 mol kg^{-1} and thereafter decreases. Hence, until the salt concentration becomes that value, charge carrier mobility is not a dominant factor for controlling conductivity. It should therefore be the charge carrier concentration which affects the conductivity up to the salt concentration of 0.85 mol kg^{-1} . After that value, mobility of the charge carriers becomes dominant with further increase of viscosity. In other words, until the salt concentration reaches 0.85 mol kg^{-1} , the carrier concentration governs the conductivity of the system while above that value, mobility takes over the control. Furthermore, the formation of ion pairs may affect the conductivity

above the concentration of 0.85 mol kg^{-1} . The dominant influence of viscosity on ionic mobility resulting conductivity reduction has also been reported in literature [3].

The temperature dependence of conductivity is shown in Fig. 3. All electrolytes exhibited a curve line indicating the typical VTF behaviour. VTF parameters are given in Table 1.

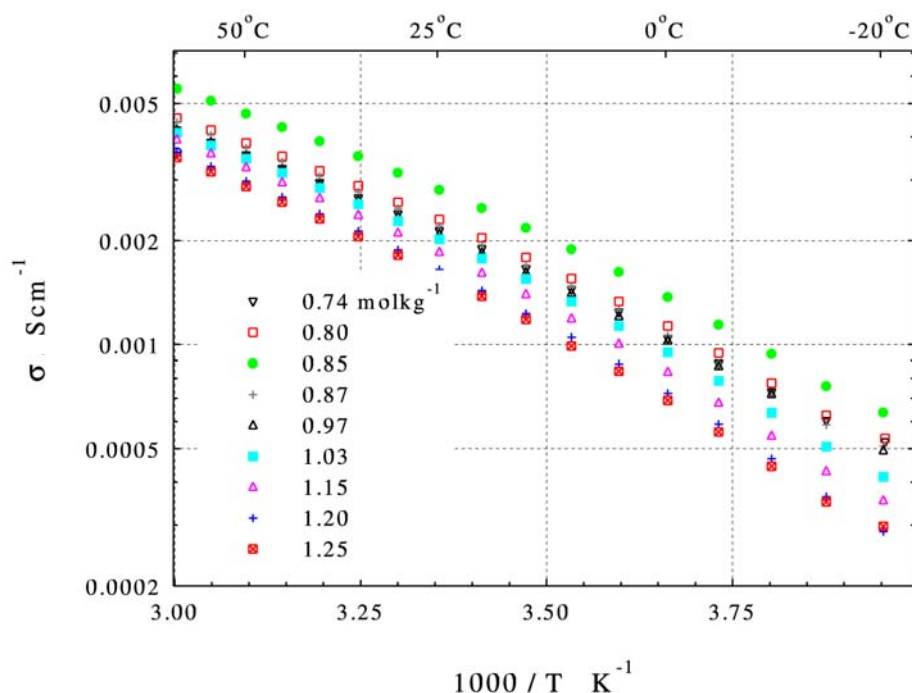


Fig. 3 VTF behaviour of the liquid electrolyte samples

VTF behavior is somewhat surprising as it is usually believed that liquid electrolytes follow Arrhenius behavior. However, some authors have reported VTF behaviour for liquid electrolytes as well [4,5].

4. CONCLUSION

The maximum RT conductivity of $2.80 \times 10^{-3} \text{ S cm}^{-1}$ could be obtained at the salt concentration of 0.85 mol kg^{-1} . Up to that concentration, conductivity enhancement is governed by the charge carrier concentration. After that, ion pairing as well as viscosity which reduce the ion mobility control the conductivity.

Table. 1 VTF parameters of the liquid electrolytes

σ_{25} (S cm ⁻¹)	A (S cm ⁻¹ K ^{1/2})	E _a (eV)	T ₀ (K)	Molality (mol kg ⁻¹)
2.13 x 10 ⁻³	2.32	0.059	134	0.74
2.37 x 10 ⁻³	2.38	0.056	138	0.80
2.80 x 10 ⁻³	3.29	0.059	134	0.85
2.21 x 10 ⁻³	2.31	0.056	141	0.87
2.12 x 10 ⁻³	4.35	0.077	112	0.97
2.00 x 10 ⁻³	2.53	0.059	139	1.03
1.85 x 10 ⁻³	3.16	0.064	136	1.15
1.64 x 10 ⁻³	2.80	0.062	141	1.20
1.60 x 10 ⁻³	2.67	0.061	142	1.25

ACKNOWLEDGEMENTS

Our sincere thanks are due to Prof. Steen Skaarup and Prof. Keld West at Technical University of Denmark for their guidance. We wish to acknowledge International Program for Physical Sciences (IPPS), Uppsala, Sweden for offering financial assistance by means of fellowships and equipment.

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