



Characterization And Development Of Plasticized Pmma Solid Polymer Electrolytes

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ABSTRACT

The focus on the Polymer electrolyte films prepared from poly (methyl methacrylate) and LiBF₄ with different concentrations of plasticizer (DBP) are described. The formation of polymer-salt complex has been confirmed by FTIR spectral studies. The temperature dependence of conductivity of polymer films seems to obey the VTF relation. Values of conductivities of the polymer complexes are presented and discussed (S. Rajendran and T. Uma, 2000). It will be used in coming future, in different field.

Key words: PMMA-LiBF₄-DBP, Polymer electrolyte, FTIR, impedance studies.

INTRODUCTION

The ongoing efforts to replace liquid electrolyte have led to the development of polymer electrolyte battery. Polymer electrolyte battery is not only well-known for its safety features but for its high power density, flexibility, plasticity of size and shape (Scrosati 2001; Vincent et. al 2000). In addition, it also plays a key role as binder for the electrode as it simplifies the fabrication process of battery cell. It is anticipated that the reduction in power consumption of electronics devices and a thin film like solid polymer electrolyte will be adequate to power these devices. However, with the advancement of technology, the hunger for higher power density in portable electronics devices such as hand-phone has led to the requirement of high power consumption as a result of increasing functionality. Many strategies and approaches have been deployed to increase the ionic conductivity such as plasticizing the polymer electrolyte with small organic molecules e.g. ethylene carbonate (EC) or dimethyl carbonate (DMC) which has high dielectric constant and low vapor pressure to address such need. However, minimal research on biodegradable polymer electrolyte is reported for the past decade. One of the primary concerns that discourage research in polymer electrolyte is believed to be due to the environmental impact it would bring if polymer electrolytes are used in large amounts (Wright 1975). To address such concern, research on developing biodegradable polymer electrolyte using 'ecomaterials' have become increasingly important with the aim to reduce the environmental impact (Fonseca, et. al 2006).

Today, LIBs represent a multibillion-dollar industry as the power supply of cellular phones, tablets, laptops, and other hand-held electronic devices. The currently used LIBs are composed of a liquid electrolyte, which is a mixture of a lithium salt dissolved in an organic solvent, sandwiched between two lithium-intercalating electrodes. Despite their high ionic conductivity, liquid electrolytes are incompatible with lithium metal with many safety issues. Presently the most difficult challenge to the development of lithium metal batteries (LMBs) stems from the uneven dendritic lithium electrode position on the negative electrode (Lin et. al 2017, Bouchet & Batteries 2014). Once nucleated, the growing dendrites have at least two harmful consequences on battery operation. First, the high surface area structures continuously react with the electrolyte solvent to form solid electrolyte interface, consuming the electrolyte and eventually causing premature battery failure. Second, dendrites eventually short circuit the battery cell, as they create an electron-conductive connection between the two electrodes. When a flammable electrolyte is used, the dendrite-induced short is both a potential fire and explosion hazard, leading to catastrophic battery failure (Tarascon & Armand 2001).

Polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable with that of common liquid ionic solutions. The development of polymer electrolytes has drawn the attention of many researchers in the last three decades as they find applications not only in lithium batteries but also, in other electrochemical devices such as super capacitors and electro chromic devices, etc. These polymer electrolytes have several advantages over their liquid counter parts. The advantages of these electrolytes include such as no internal shorting, leakage of electrolytes and non-combustible reaction products at the electrode surface existing in the liquid electrolytes (Gray 1991, Scrosati 1993, Gray 1997, Mac Callum & Vincent 1987, Mac Callum & Vincent 1987).

In an attempt to look for good lithium ion conducting polymer electrolytes, a new plasticized polymer electrolyte composed of PMMA as the host polymer, LiBF₄ as a salt and dibutyl phthalate (DBP) as a plasticizer has been studied. The ionic conductivity of these gels at room temperature is of the order of 10⁻³ to 10⁻⁴ S cm⁻¹ and is comparable with values reported for similar systems.

EXPERIMENTAL

Thin films of PMMA–LiBF₄–DBP in different mole ratios were prepared by solution cast technique. PMMA with an average molecular weight of 1×7 × 10⁵ (Aldrich) and LiBF₄ (Aldrich) were dried by heating them under vacuum at 100 and 70°C for 12 and 24 h, respectively. DBP (dibutyl phthalate) (Aldrich) was used without further purification. The appropriate weights of PVC and LiBF₄ (table 1), were dissolved in THF (tetrahydrofuran) followed by the addition of plasticizer. The solution was then stirred continuously until the mixture took a homogeneous viscous liquid appearance. The solutions of different compositions were poured into identical Teflon moulds and THF was allowed to evaporate in air at room temperature. This procedure provided mechanically stable, free-standing and flexible films with thickness between 110–200

mm. The films formed were again dried in a vacuum oven at 323 K with a pressure of 10^{-3} torr for 24 h. Impedance of the film was studied over the frequency range 40 Hz–100 kHz using a LCZ meter (Model 3330, Keithley Instruments Inc., USA). The conductivity was obtained from the bulk resistance found in the complex impedance diagram (fig. 2). Perkin-Elmer Paragon 500 Grating IR spectrophotometer was used for IR measurement.

RESULTS AND DISCUSSION

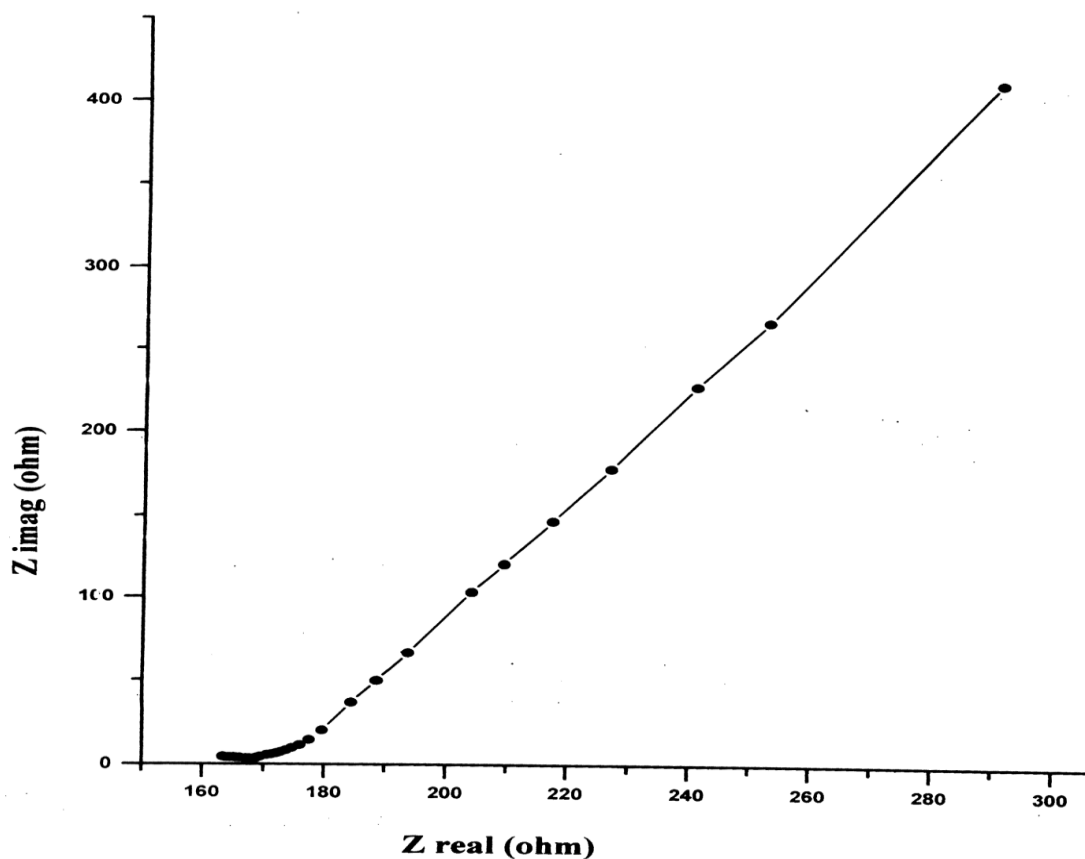
FTIR SPECTROSCOPIC STUDIES:

The infrared spectra of PMMA, LiBF₄, DBP and polymer complexes are shown in figure 1. IR would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase. The absorption peaks of PMMA (2927, 1559, 1458, 1384, 990, 840, 750 and 483 cm⁻¹), LiBF₄ (3563, 1633, 1305, 1083 and 521 cm⁻¹) and DBP (2961, 2874, 1728, 1578, 1385, 1120 and 1038 cm⁻¹) get shifted in the polymer complexes. The vibrational bands of PMMA (3446 and 668 cm⁻¹) and DBP (3435 cm⁻¹) are found to be absent in the polymer complexes.

Table 1: Conductivity values of PMMA–LiBF₄–DBP polymer complexes

Film	Polymer complex	σ values ($\times 10^{-3}$ S cm ⁻¹)					
		304 K	328 K	338 K	348 K	358 K	373 K
F1	10–5–85	4.538	6.262	7.162	9.865	14.797	73.987
F2	15–5–80	2.493	5.232	5.717	7.848	10.464	12.556
F3	25–5–70	1.649	3.737	4.312	4.359	4.671	5.096
F4	35–5–60	0.327	0.862	1.221	1.832	2.093	2.349

Fig. 1: FTIR plots for PMMA, LiBF₄, DBP and the complexes: (a) PMMA: (b) LiBF₄: (c) DBP: (d) PMMA–LiBF₄–DBP (10–5–85 mole%): (e) PMMA–LiBF₄–DBP (15–5–80 mole%): (f) PMMA–LiBF₄–DBP (25–5–70 mole%): (g) PMMA–LiBF₄–DBP (35–5–60 mole%)



The peaks at 2927 and 1734 cm^{-1} are assigned to C-H stretching and C=O stretching vibrations, respectively in PMMA. The peaks at 2953, 1731, 1485 and 1247 cm^{-1} are assigned to C-H stretching, C=O stretching, CH₂- stretching and O-CH₃ stretching vibrations, respectively in the polymer electrolyte systems (Vien et. al 1991). The above analysis establishes the formation of polymer-salt complexes.

CONDUCTIVITY MEASUREMENTS:

The conductivity values of PMMA-LiBF₄-DBP systems are given in table 1. (Iijima et. al 1985) reported the conductivity value as $10^{-3} \text{ S cm}^{-1}$ at 25°C for PMMA based system with an average molecular weight of 7000. (Bohnke et. al (1993) dissolved PMMA, up to 20 weight% in a LiClO₄ (1M)-PC electrolyte at room temperature to obtain a homogeneous and transparent gel. They reported that the resulting gel electrolyte possessed a conductivity of $2 \times 3 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C. (Sekhon et. al (1998)) reported the ionic conductivity for PMMA-LiCF₃SO₃-PC-EC polymer electrolytes in the range 0.6×10^{-3} to $5.5 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature.

In the present work, the conductivity value of PMMA-LiBF₄-DBP system (film F1) is found to be $4.5 \times 10^{-3} \text{ S cm}^{-1}$ at 304 K (table 1). This value compares well with those values already reported (Bohnke et. al 1993; Sekhon et. al 1998). The presence of the high molecular weight PMMA imparts a very high macroscopic viscosity ($\gg 335 \text{ Pas}$) to the system without significantly diminishing the conductivity, i.e. the conductivity of the gel remains very close to that of a liquid electrolyte. It is concluded that PMMA acts

primarily as a stiffener that fast ion transport occurs through a continuous conduction path which does not affect the electrochemical stability of the electrolyte. In later studies, (Bohnke et. al (1993) revealed that the ionic conductivity of PMMA–LiClO₄ (1 M)–PC system decreases with increasing amount of polymer and lies between 5×10^{-3} and 5×10^{-5} S cm⁻¹ at room temperature.

In the present investigation, the conductivity values for PMMA–LiBF₄–DBP are found in the range $4 \times 5 \times 10^{-3}$ – $3 \times 3 \times 10^{-4}$ S cm⁻¹ for various mole ratios of PMMA and DBP (table 1) at 304 K. It is seen from table 1, that the conductivity decreases with increase in concentration of PMMA. This behaviour is also reported by (Bohnke et. al (1993). It is also observed that the conductivity increases with concentration of DBP. This may be due to the lowering of viscosity with increasing plasticizer concentration. It is also observed from table 1 that as the temperature increases, conductivity values also increase for all the compositions. This behaviour is in agreement with theory (Armand et. al 1979).

Figures represent the Arrhenius plot of the ionic conductivity for the polymer electrolytes. The overall features of the Arrhenius plot are quite similar for the electrolyte systems that no linear dependence could be obtained seems to suggest that ion conduction follows the Williams Landel–Ferry (WLF) mechanism (Williams et. al 1955). In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion (Okamoto et. al 1993). Thus, the results may be more effectively represented by the empirical Vogel–Tamman–Fulcher (VTF) equation (Vogel 1922; Fulcher 1925; Tamman and Hesse 1926).

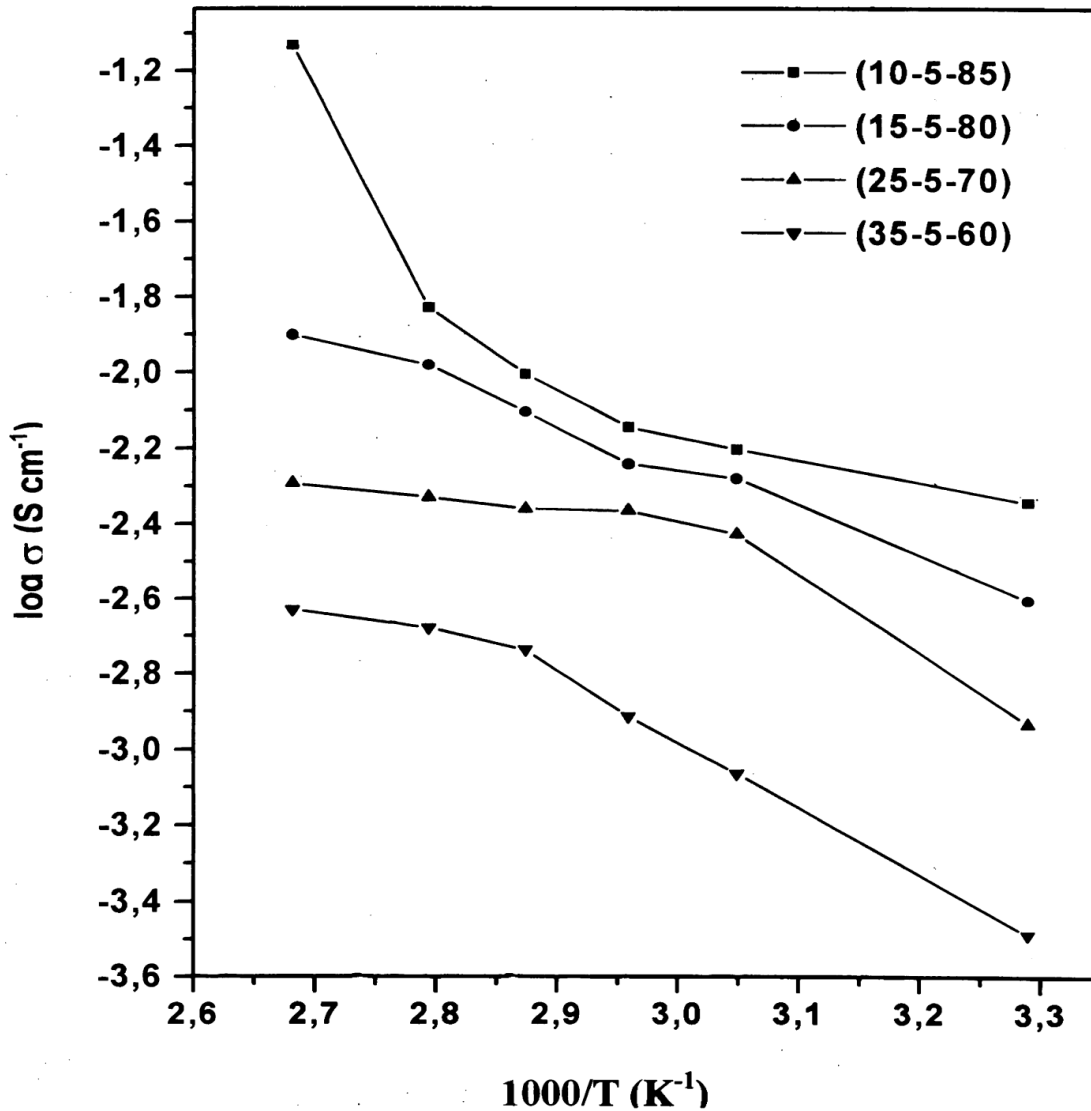


Fig. 2: Arrhenius plot of log conductivity against reciprocal temperature for PMMA-LiBF₄-DBP polymer complexes: (a) PMMA-LiBF₄-DBP (10-5-85 mole%): (b) PMMA-LiBF₄-DBP (15-5-80 mole%): (c) PMMA-LiBF₄-DBP (25-5-70 mole%): (d) PMMA-LiBF₄-DBP (35-5-60 mole%).

$$\sigma = AT^{-1/2} \exp(-B/T-T_g),$$

Where A and B are constants and T_g the reference temperature taken as the glass transition temperature here. Constant A in the VTF equation is related to the number of charge carriers in the electrolyte system and constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. It supports the idea that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e. plasticizer-rich phase, involves the plasticizer, the salt and PMMA, the characteristics of the viscous matrix are brought out.

CONCLUSION:

It is complex formation in PMMA–LiBF₄–DBP system have been confirmed from IR studies. The ionic conductivity more increases with the concentration of plasticizer. The conductivity more greatly changes from 10⁻⁴ to 10⁻³ S cm⁻¹ as like the mole ratio of DBP increased from 60 to 85. That may be due to the lowering of viscosity with increased plasticizer concentration.

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