

UNIVERSITI TEKNOLOGI MARA

**EFFECTS OF ADDITION OF
BMIMCF₃SO₃ IONIC LIQUID ON
ELECTRICAL, THERMAL AND
STRUCTURAL PROPERTIES OF
PVC-LiCF₃SO₃-BMIMCF₃SO₃
POLYMER ELECTROLYTE**

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ABSTRACT

In this study, poly(vinyl) chloride (PVC) is used as polymer host, lithium triflate (LiCF_3SO_3) as doping salt, and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($\text{BMIMCF}_3\text{SO}_3$), an ionic liquid is used as plasticiser for preparation of plasticised polymer electrolyte $\text{PVC-LiCF}_3\text{SO}_3\text{-BMIMCF}_3\text{SO}_3$. The polymer electrolytes were prepared by using solution cast technique. Characterisation techniques of EIS, XRD, DSC, FTIR, and TNM were used to study the properties of the PVC-based electrolyte. Conductivity for pure PVC at room temperature is found to be $5.23 \times 10^{-10} \text{ Scm}^{-1}$. A system composed of PVC with just ionic liquid which served as a control, recorded conductivity of $1.50 \times 10^{-9} \text{ Scm}^{-1}$. The conductivity of PVC rose to $1.07 \times 10^{-8} \text{ Scm}^{-1}$ upon addition of LiCF_3SO_3 , which is an increase of about two orders of magnitude. Further increase of ionic conductivity is obtained when ionic liquid is added to the salted system. The highest conductivity achieved is $1.12 \times 10^{-7} \text{ Scm}^{-1}$ for 3 wt.% of ionic liquid. The increment of conductivity is attributed to increase in number of mobile ions as evidenced by deconvolution of FTIR and decrease in crystallinity of the films as evidenced by XRD, while DSC indicates that the system is more flexible due to the plasticising effect of ionic liquid. Temperature dependence of conductivity study showed that the system $\text{PVC-LiCF}_3\text{SO}_3\text{-BMIMCF}_3\text{SO}_3$ increased in conductivity up to its T_g value after which it decreased. This is attributed to the presence of ionic liquid which implies that motion of polymer segments are limited where ions are triggered by hopping mechanism at temperatures below T_g and at temperatures above T_g , cations were reduced to particles. Transference number of this system is found to be ~ 0.92 .

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CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

Ion conducting solid polymer electrolytes have been added with plasticiser to enhance their conductivity. Normally conventional plasticisers which have high dielectric constant and low viscosity such as ethylene carbonate (EC), propylene carbonate (PC), dimethylformamide (DMF), etc. is used. Recently, ionic liquids have been used instead. This approach has been found to enhance the conductivity, electrochemical stability and mechanical stability of the polymer electrolytes (Saroj et al., 2012; Nath and Kumar, 2014).

Polymer electrolytes incorporated with ionic liquid reported in the literature come in many different forms. Saroj and co-workers (2013) worked on PVP+EMIMBF₄ binary polymer electrolyte prepared by solution cast technique. The ionic conductivity obtained is $1.58 \times 10^{-7} \text{ Scm}^{-1}$ at 60°C for 25 wt.% concentration of EMIMBF₄. According to these authors the conductivity increased due to plasticising effects of EMIMBF₄, which increased the amorphous nature of the electrolyte. Since no salt is added in this polymer electrolyte, it is thus acknowledged that the ionic liquid contributes the ions. They also reported that cation of the ionic liquid which is EMIM⁺ complexed with oxygen of the side group N-C=O of PVP, thus supporting that ionic conductivity has increased because of plasticising effects of EMIMBF₄ (Saroj et al., 2013).

Higher conductivity values of $1.20 \times 10^{-3} \text{ Scm}^{-1}$ at 25°C were reported in another literature (Fisher et al., 2011). These authors prepared ternary polymer electrolyte system of PEO-LiTFSI-S₂TFSI by solution cast technique. They attributed the increase in conductivity to increase in chain mobility. The authors did not report any interaction in the polymer electrolyte and so the types of ion involved in conduction could not be identified (Fisher et al., 2011).

In a recent work, conductivity values of $4.46 \times 10^{-3} \text{ Scm}^{-1}$ at 30°C for 50 wt.% ionic liquid is reported for ternary polymer electrolyte system of PVA-NH₄COOCH₃-BMIMCl. The authors provided evidence of complexation between the components