J Polym Res (2014) 21:381
DOI 10.1007/s10965-014-0381-z

ORIGINAL PAPER

The effect of carbonate-phthalate plasticizers on structural, morphological and electrical properties of polyacrylonitrile-based solid polymer electrolytes

W. G. Chong · Z. Osman

Received: 17 October 2013 / Accepted: 10 February 2014

Abstract Polyacrylonitrile (PAN) based solid polymer electrolyte consisting lithium tetrafluoroborate ($LiBF_4$), ethylene carbonate (EC) and dimethyl phthalate (DMP) have been prepared using solution casting method. Comparative studies were done on unplasticized PAN-$LiBF_4$ system and the PAN plasticized system with the novel binary plasticizers of EC and DMP in the ratio of 1:1 by the variation of $LiBF_4$ concentration. The highest room temperature conductivity of electrolyte in PAN-$LiBF_4$ system is 1.83×10^{-3} S cm^{-1} while 1.08×10^{-2} S cm^{-1} is obtained from PAN-EC-DMP-$LiBF_4$ system. The complexation and structure of polymer electrolytes have been investigated as function of $LiBF_4$ content at different weight percentages. The morphology and crystalline phase of polymer host is completely changed on the addition of salt and plasticizers. The fraction of free ions is greatly dependent on the amount of salt and the presence of plasticizers.

Keywords Polyacrylonitrile · Phthalate · Ionic conductivity · FESEM · XRD · FTIR spectroscopy

Introduction

The area of polymer electrolytes has attracted considerable interest since polyethylene oxide (PEO) based polymer electrolyte was first discovered by Wright and co-workers who have brought out the technological significance to the development of the energy resources [1–3]. Ionic conduction is generally associated with liquids, either solvents with high dielectric constants or molten salts. However, solids that can function as electrolytes also known as solid electrolytes with typical conductivity value ranging from 10^{-6} to 10^{-1} S cm^{-1} are interesting due to their wide ranging applications such as gas sensors [4, 5], electrochemical display devices [6, 7], power sources [8], fuel cells [9], solid state high energy density batteries [10] and so on. Besides the advantage of flexibility, polymers can also be cast into films of desired thickness. Many approaches were done in order to develop a polymer electrolyte with good ionic conductivity lead to the evolution of polymer electrolyte from a simple solid polymer electrolyte (SPE) to different forms such as plasticized polymer electrolytes, polymer blends, composites, gel and ionic liquids contained electrolyte [11–15]. Keeping pace with the requirement for more advanced application, a new class of polymer electrolyte namely hybrid inorganic-organic polymer electrolytes has been developed which existing in mono-phase and multi-phase was reported by Noto et al. [16]. Polyacrylonitrile (PAN) based polymer electrolytes carry high conductivity values ranging from 10^{-3} to 10^{-2} S cm^{-1} at room temperature which is close to the value of commercial liquid electrolyte [17, 18]. Incorporation of plasticizers was found to be useful in reducing the crystalline region of the polymer which in turns effectively improves the ionic conduction. However, no single plasticizer exhibits the perfect balance of properties for every application. Ethylene carbonate (EC) is an indispensable solvent due to its high dielectric constant. It was reported that the presence of EC aids the formation of effective protective film (SEI) on a graphitic anode [19]. The advantages of binary solvent was discovered by Pistoia and co-workers [20] that good combination of solvents not only improve the ion dissociation, the mixture balancing their unique characteristics and at the same time improve the interfacial properties. Phthalates are used in virtually every major product category such as construction, household products, packaging and medical products [21]. Dimethyl phthalate (DMP) helps to reduce the crystalline phase of the polymer chains and the electron rich carbonyl group of DMP aiding the

W. G. Chong · Z. Osman (✉)
Physics Department, University of Malaya,
50603 Kuala Lumpur, Malaysia
e-mail: zurinaosman@um.edu.my

Published online: 23 February 2014