

Material Properties

Structure and ion transport in an ethylene carbonate-modified biodegradable gel polymer electrolyte

Ravi Muchakayala^a, Shenhua Song^{a,*}, Shang Gao^a, Xiaoling Wang^b, Youhua Fan^a^a Shenzhen Key Laboratory of Advanced Materials, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen 518055, China^b Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

ARTICLE INFO

Article history:

Received 29 October 2016

Accepted 12 December 2016

Available online 23 December 2016

Keywords:

Gel polymer electrolytes

Structural studies

Ion transport

Ionic conductivity

Transference number

Electrochemical stability

ABSTRACT

The influence of ethylene carbonate (EC) addition on 85poly(ϵ -caprolactone):15Lithium thiocyanate (85PCL:15LiSCN) polymer electrolyte is investigated using X-ray diffraction, impedance spectroscopy, Wagner's polarization and electrochemical measurements. The results reveal that the amorphicity of the 85PCL:15LiSCN system increases with increase of EC content up to an optimal level of 40 wt.%. This is reflected in the electrical properties of the gel polymer electrolytes, i.e., the 40 wt.% EC-incorporated gel polymer electrolyte exhibits both high amorphicity and high electrical conductivity as compared to the other samples. The EC concentration dependences of dielectric constant and electrical conductivity show a similar trend, indicating that these properties are closely related to each other. The total ionic transference numbers of EC-incorporated gel polymer electrolytes are in the range 0.989–0.993, demonstrating that they are almost completely ionic conductors. The electrochemical stability window of the 40 wt.% EC-incorporated gel polymer electrolyte is ~ 4.1 V along with the electrical conductivity of $2.2 \times 10^{-4} \text{ S cm}^{-1}$, which is significantly improved as compared to the 85PCL:15LiSCN system (3.0 V and $1.04 \times 10^{-6} \text{ S cm}^{-1}$). Consequently, the addition of EC in the 85PCL:15LiSCN polymer electrolyte leads to a promising improvement in its various properties.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Solid polymer electrolytes (SPEs) have been attracting great interest worldwide due to their wide range of applications such as lithium batteries, organic solar cells, supercapacitors and electrochromic display devices. They also offer abundant advantages such as leakage-proof, light weight, improved safety, inexpensive, good thermal stability, high flexibility and ease of fabrication into required shapes and sizes [1,2]. Most of the investigations concentrated on polymers such as poly(vinyl chloride) (PVC), poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), poly(vinyl pyrrolidone) (PVP) and poly(vinylidene fluoride) (PVDF) [3–9] which are used as host polymers for developing different solid polymer electrolyte films. These host polymers are not biodegradable and impose several ecological issues, e.g., global warming and large wastages. Obviously, the use of environment-friendly biodegradable materials for the development of complexed polymer

electrolytes would help mitigate the environmental issues. Therefore, many efforts have been made recently to develop biodegradable polymer electrolytes by using various biodegradable polymers as host materials, such as starch, cellulose, polyvinyl alcohol (PVA), chitosan and poly(ϵ -caprolactone) (PCL) [10–14]. Among these polymers, polyester-based biodegradable poly(ϵ -caprolactone) is one of the most promising host materials because of its unique structure. It has the ability to coordinate with ions and provides new sites for fast ion transport. Poly(ϵ -caprolactone) is environment-friendly and nontoxic. Hence, it is widely used in biomedical and tissue engineering industries [15,16]. Due to its low glass transition temperature, the polymer chains are flexible and exhibit segmental motion, which helps ion transport between two complexation sites [17,18]. Hence, PCL was selected in this study as a promising host polymer for preparation of polymer electrolyte films. Lithium salts are commonly used as dopants in complexed polymer electrolytes (i.e., polymer doped with lithium salt) due to its low atomic radius, low lattice energy and cost, etc. Several researchers reported PCL-salt-complexed polymer electrolytes with their maximum room-temperature electrical conductivity values being (i) $1.1 \times 10^{-7} \text{ S cm}^{-1}$ for the 88PCL:12LiBF₄, (ii)

* Corresponding author.

E-mail addresses: shsong@hitsz.edu.cn, shsonguk@aliyun.com (S. Song).

$1.3 \times 10^{-6} \text{ S cm}^{-1}$ for the 90PCL:10LiClO₄, (iii) $3.6 \times 10^{-5} \text{ S cm}^{-1}$ for the 90PCL:10LiCF₃SO₃ [19], (iv) $4.6 \times 10^{-8} \text{ S cm}^{-1}$ for the 74PCL:26NH₄SCN [20], and (v) 6.3×10^{-7} for the 60PEO:15PCL:25LiClO₄ [21]. From the reported results, the maximum electrical conductivity value obtained at ambient temperature is $\sim 10^{-5} \text{ S cm}^{-1}$, which is not high enough for ionic device applications. Therefore, enhancing the electrical conductivity via different approaches has been considered, such as polymer blending, incorporation of nano-fillers, co-polymerization, cross-linking, and plasticization [22–26]. One of the most effective methods is plasticization. In this process, the low molecular weight plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) are incorporated into the salt-complexed system. These plasticizers may considerably increase the electrical conductivity of the complexed polymer electrolytes [27,28]. The plasticizer-incorporated polymer electrolytes are termed gel polymer electrolytes, which possess the properties of both solid and liquid electrolytes.

Ethylene carbonate (EC) has a high dielectric constant (89.8) along with good compatibility with many polymers. Hence, it was preferably chosen as a plasticizer in the present study in order to raise the electrical conductivity of a 15 wt.% lithium thiocyanate-complexed PCL system, i.e., the 85PCL:15LiSCN system. The use of a polymer electrolyte in practical device applications is dictated by its room-temperature electrical conductivity, ionic transference number and electrochemical stability window. Accordingly, this study focuses on the aforementioned characteristics of the EC-incorporated biodegradable polymer electrolyte. It is expected that the findings from this study will make good contributions to understanding of the EC effect on the complex polymer electrolyte.

2. Experimental details

Poly(ϵ -caprolactone) (PCL) with $M_n = 80 \text{ kDa}$ and lithium thiocyanate (LiSCN) with molecular weight 65.02 g/mol (99% purity) were obtained from Sigma Aldrich and used as the host polymer and dopant salt, respectively. Ethylene carbonate (EC) was purchased from Aladdin Marketing and used as the plasticizer. Three dimensional chemical structures of PCL, LiSCN and EC are shown in Fig. 1 [29]. The 85PCL:15LiSCN + EC gel polymer electrolyte systems were prepared by conventional solution casting. In terms of our previous study [30], the 85PCL:15LiSCN system was identified as the optimal composition, i.e., this composition gave a stable film with high amorphicity and electrical conductivity. The optimized quantities of PCL and LiSCN were separately dissolved in chloroform, and then mixed together under magnetic stirring at 40 °C for 5 h to acquire a mixed solution. Different quantities of EC were added to the mixture, and then stirring was continued for 12 h to obtain a homogeneous solution. Finally, the obtained solutions were cast over glass petri dishes and the chloroform was allowed to

evaporate at ambient temperature to get free standing films. The thickness of these films was determined to be approximately 120 μm by a micrometer. The prepared gel polymer electrolyte film, as shown in Fig. 2, was semitransparent in nature and mechanically stable, i.e., it did not crack after appreciable bending.

X-ray diffraction (D/max Rigaku X-ray diffractometer with Cu K α radiation) was employed to study the crystal structures of the gel polymer electrolyte (GPE) films. The surface morphologies of the polymer films were observed using optical microscopy (OM).

Mechanical properties of the PCL based polymer electrolyte films were evaluated using a universal testing machine (CMT7504, China) at room temperature. A film sample with a size of 10 mm \times 80 mm (width \times gauge length) was tensile-deformed until fracture under a crosshead speed of 5 mm min⁻¹. The thickness of the film was measured with a digital micrometer at different locations and the mean value taken as the nominal thickness of the film for the calculation of mechanical properties. Thermal measurements of the polymer electrolyte films were performed using an STA 449F3 Jupiter thermal analyzer under a nitrogen atmosphere in the temperature range of 50–700 °C at a heating rate of 10 °C min⁻¹.

The electrical conductivity of the polymer films were measured using an impedance analyzer (PSM 1735) in the frequency range of 1 Hz – 1 MHz. In this technique, the GPE film was cut into a circular

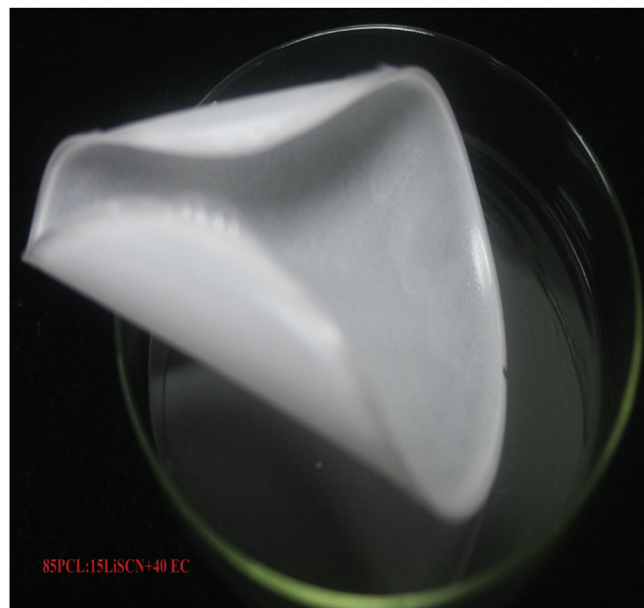


Fig. 2. Photomicrograph of gel polymer electrolyte film.

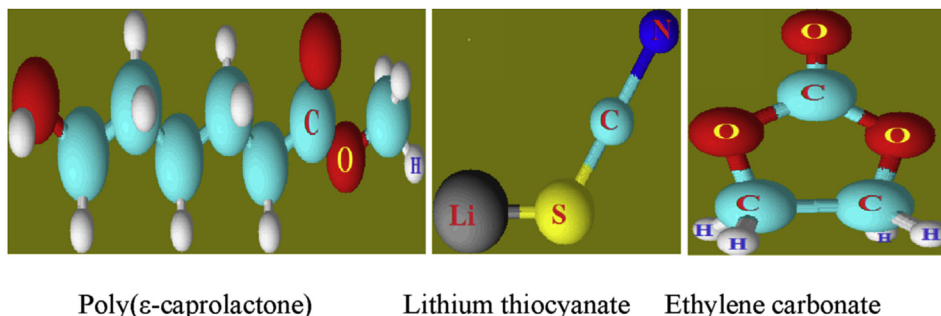


Fig. 1. Three dimensional structural representation of poly(ϵ -caprolactone) (PCL) Lithium thiocyanate (LiSCN) and Ethylene carbonate (EC) [29].

Download English Version:

<https://daneshyari.com/en/article/5205675>

Download Persian Version:

<https://daneshyari.com/article/5205675>

[Daneshyari.com](https://daneshyari.com)