



Lithium ion conduction in corn starch based solid polymer electrolytes



K.H. Teoh, Chin-Shen Lim, S. Ramesh*

Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

A series of various compositions of corn starch and lithium perchlorate (LiClO₄) polymer electrolyte thin films were prepared by solution casting technique. The optimum ionic conductivity of 1.28×10^{-4} S/cm was achieved by the composition ratio of 40 wt.% LiClO₄ and 60 wt.% corn starch at 353 K. Dielectric behavior was analyzed using dielectric constant (ϵ'), dielectric moduli (M'') and dissipation factor ($\tan \delta$) of the samples. The complex permittivity reveals the presence of dipoles in the bulk materials. The complexation between the corn starch and LiClO₄ in the matrix polymers are proven based on the presence of the change in intensity, shape of peaks and shift in peaks as observed in Fourier transform infrared spectroscopy (FTIR) analysis. Surface morphology and thermal properties of the film was carried out with scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

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1. Introduction

In recent times solid polymer electrolytes (SPEs) have been of great interest due to its wide range of application and ease of preparation as polymer film. However, conventional synthetic polymers usually originate from petroleum and most are regarded as non-degradable. In view of this, numerous works have been dedicated to synthesize biodegradable polymer electrolytes with high ionic conductivity [1,2]. This is believed to be a great alternative to synthetic-based polymer electrolytes which would greatly reduce the impact on the environment. Starch is chosen in this study as it is a naturally occurring polymer where a large number of linear amylase and branched amylopectin is bonded together with glycosidic bond. Furthermore, starch is highly biodegradable [3], possess good solubility properties, low cost, obtained in abundance and is a renewable material. Numerous investigations have been carried out to develop a mechanically stable and high

ionic conductivity corn starch based polymer electrolyte to replace the conventional type [4]. Starch blended with synthetic polymer poly (vinyl alcohol) (PVA) has been studied as potential biodegradable polymer [5]. Xiong et al. reported that the blend of PVA with corn starch with the addition of nano silicon dioxide (nano-SiO₂) greatly increased the water resistance and mechanical properties of the film [6].

Lithium perchlorate (LiClO₄) is comprised of a small sized cation and a large sized anion. The ionic conductivity is affected by the diffusion rate of ions which depends on the size of the ion. LiClO₄ is chosen due to its good conductivity [7]. LiClO₄ is more favorable compared to other lithium salts due to the low interfacial resistance when lithium metal was used as anode. Moreover, LiClO₄ has high dissociation energy, thus it is readily soluble in most solvents. As reported by Jo et al. the utilization of LiClO₄ as salt shows high ionic conductivity and wide electrochemical window up to 4.9 V [8]. Furthermore, an average of 4.0 V of electrochemical stability window has been achieved by various researchers [9,10]. It is expected that LiClO₄ is a promising materials as a lithium salt for a lithium polymer battery.

* Corresponding author. Tel.: +60 3 79674146.

E-mail address: rameshtsubra@gmail.com (S. Ramesh).

The utilization of distilled water as solvent functions as a plasticizer as well. Water is crucial in the gelatinization process as it disrupts the granular structure causing starch molecules to dissolve [6]. These interactions are Van der Waals forces which make water function as an agent of polymer network formation [11]. Furthermore, water is chosen due to its non-toxicity, good solubility and excellent compatibility which also promote green energy to the world.

In this work, studies have been carried out to investigate the composition effect of LiClO_4 in corn starch based solid polymer electrolytes. To our knowledge, no dielectric studies have so far been reported for polymer electrolyte based on corn starch. The work focuses on the preparation of SPEs from corn starch and lithium perchlorate. The SPEs were characterized by AC impedance spectroscopic studies to study the conductivity and dielectric properties. The complex interaction between the corn starch and LiClO_4 salt was studied by FTIR. Surface morphology and thermal properties of the film was carried out with scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental

Corn starch with a linear formula of $\text{C}_6\text{H}_{10}\text{O}_5$ was obtained from Sigma–Aldrich. Lithium Perchlorate, LiClO_4 , with 99.99% purity and less than 100 ppm total metallic purities was obtained from Aldrich. The solution was stirred overnight to ensure complete dissolution of the polymer–salt. The thin films were prepared by solution casting technique with distilled water as solvent. Designation of various compositions is tabulated in Table 1. Morphology of polymer electrolyte was studied by using Leica's SEM (model S440) at an acceleration potential of 8 kV at room temperature. Images were captured by automatic image capturing software. Magnifications are as indicated at the bottom of each figure. The sample were cut and sandwiched between two stainless-steel blocking electrodes. A HIOKI 3532-50 LCR Hi-Tester connected to a computer was used for data acquisition over the frequency range of 50 Hz to 5 MHz. The thickness of the film was measured by means of a digital micrometer screw gauge. The entire dielectric studies were measured in an isolated custom made Faraday cage to reduce any possible environmental electronic noise particularly at lower frequency measurements. FTIR studies were performed with a Thermo Scientific Nicolet IS 10 in the wave region between 4000 and 600 cm^{-1} . The resolution of the spectra obtained

at room temperature was 1 cm^{-1} . Attenuated total reflectance (ATR) sampling technique was used together with universal diamond ATR top-plate. Thermal properties were studied using TA Instrument Thermal Analyzer comprising DSC Q200. Before analysis, the samples were equilibrated at 105 °C for 5 min to remove any traces of water. The samples were then cooled rapidly to –50 °C and then reheated to 200 °C at a heating rate of 30 °C min^{-1} . Thermogravimetric analyses (TGA) were conducted with TA Q500 Thermogravimetric Analyzer under nitrogen atmosphere at a heating rate of 50 °C/min.

3. Results and discussion

3.1. Scanning electron microscopy

The grain morphology and microstructure of the samples were investigated using Scanning Electron Microscopy (SEM). Fig. 1 shows the SEM images of the prepared samples at magnification of 1000 \times . From the results, pure corn starch shows a homogeneous distribution without any impurities on the surface. However, when LiClO_4 was added, formation of rod-type crystalline on top of the corn starch surface was observed. It is obvious that the introduction of LiClO_4 plays an important role in the morphology and distribution of particles. The grain size was measured and tabulated in Table 2. CS20 shows a distribution of 50 μm grain size and CS50 shows similar crystallite shape with grain size 7.5–40 μm . The larger grain size reduced the number density of ions and reduced the ionic mobility that could be due to ion traps in the polymer electrolytes. CS30 and CS40 show smaller spherulite size and even distribution on the surface. Generally, a smaller and uniform distribution of particle sizes allows easier penetration of electrolyte and shorter pathway for Li^+ ion diffusion [12]. However, upon close inspection, CS30 and CS50 were found to have pores on the surface. This is responsible for the increase in resistance to ion diffusion within the active material. Further investigation was carried out using A.C. impedance spectroscopy.

3.2. Alternating current (AC) impedance studies

In order to understand how the ion transport was affected by grain size in polymer electrolyte, further analysis with impedance spectroscopy was required. In principle, the overall resistance of polymer electrolyte is composed of bulk resistance R_b and charge transfer resistance R_{ct} . Fig. 2 represents the nyquist plot for all the samples and equivalent circuit inset for CS50. The steep capacitive impedance rises in the low frequency region accompanied with high frequency semicircular features owing to the bulk and interfacial properties. The locus of the semicircle intercepts the real axis at R_b and R_{ct} as shown in the nyquist plot. Following the semicircle with decreasing frequency, the plots transform to a slopping line. A Warburg element Z_w is introduced in the circuit to emphasize the solid state diffusion of Li-ions in the active materials corresponding to the slopping line. Constant phase element has

Table 1

Designation for various composition of corn starch– LiClO_4 polymer electrolyte.

Composition of corn starch: LiClO_4 (wt.%)	Designation
100:0	CS0
90:10	CS10
80:20	CS20
70:30	CS30
60:40	CS40
50:50	CS50

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