Biopolymer electrolyte from Pectin doped with lithium salts and plasticizer for lithium ion batteries

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Abstract:

Recent in-depth efforts in developing solid polymer electrolytes that enable commercially practicable lithium metal electrodes for lithium- ion batteries remain challenging. Hence, the present study aims at developing a solid polymer electrolyte using pectin, lithium salts and plasticizers through solution casting technique. Pectin a natural polymer chain (linear) of galacturonic acid has been used as a host. Polymer host with different ratios of lithium nitrate ($LiNO_3$) salts, ethylene carbonate (EC) and succinonitrile SN plasticizers were prepared. The film sustains its structural integrity by avoiding the structural collapse due to the crystallized EC-solvent presence within its matrix. EC acts by increasing the degree of salt dissociation, also ionic mobility. The number ion pathways have also been increased that indicated these solid biopolymer electrolytes are encouraging for operation in lithium ion batteries. XRD illustrates the crystallinity is affected by the addition of salt and plasticizers, that is responsible for the ion transport which enhances the amorphous nature of the films A morphological study by laser profilometry gives the average roughness of the films. Electrochemical impedance spectroscopy (EIS) measurements suggest the suitability with 10^{-4} Scm^{-1} ionic conductivity. The thermo gravimetric analysis elucidates that the prepared electrolyte films are thermally stable. The results exhibit this solid polymer electrolyte would-be a better one for lithium ion battery systems.

Keywords: Polymer electrolyte, TGA, Laser Profilometry, Ionic conductivity, pectin, lithium nitrate.

1. Introduction

In the advancements of continuing trend on the road to miniaturization with eternal capacity, the solid polymer electrolytes overcome other electrolytes with prospective advantages addressing environmental necessities. [1]. Polymer electrolyte composite frameworks of pectin/chitosan were reported [2]. Injectable biomaterials grounded on pectin in applications of bone (tissue) engineering were also examined [3, 4]. Conversely, the main complication is the conductivity range commonly exists lower than 10^{-3} S cm^{-1} excluding those for real-world applications that fails to optimise the properties of the material required [5-9]. Enhancing safety without sacrificing the cells performance by controlling the non-flammability of electrolytes is the challenging one. [10]. Functionalization of biopolymers by modification imparts suitable properties onto them. [11]. Plasticization provides an effective salt solvation with rise in ion mobility to the matrix (polymer) with large volume and chain flexibility motion. [1]. Routes for reducing the crystallinity by adding liquid plasticizers ethylene carbonate (EC) and succinonitrile (SN) to increase the ionic conductivity is found to be efficient. Ethylene carbonate (EC) having reduced crystallinity was preferred for its superior properties mainly a high dielectric constant [1]. SN having high polarity reaches a great effect in charge separation, is expected to provide high ionic conductivity [12]. It has a lower flammability and negligible vapour pressure which is a major problem faced in electrolytes [13, 14]. Zhou et al. prepared all solid state electrolyte using SN as a plasticizer with cyano

ethyl poly (vinyl alcohol), which exhibited excellent mechanical strength and high security [15].

The present work aims in preparing Pectin- $LiNO_3$ polymer electrolytes at a number of compositions by addition of plasticizers. The effect of EC and SN in the above combination is investigated and compared. The characterizations performed are conductivity measurements, morphological study; thermal stability; FTIR and XRD analysis.

2. Experimental

Polymer electrolytes by the host polymer Pectin and lithium nitrate (Sigma Aldrich) as thin films of two sequences were prepared by solution casting technique. Pectin and $LiNO_3$ of various compositions (70:30, 60:40, 50:50, 40:60 wt. %) were prepared with distilled water as a solvent, added plasticizers Ethylene carbonate (EC) 5% to one of the series similarly 5% Succinonitrile (SN) to another series which were mechanically stirred for 24 hrs. for attaining homogenous solution. Then solution mixtures were transferred onto separate petri dishes and were placed in a hot air oven to make sure that they are completely dry. The preparations of the electrolyte films are similar with different plasticizers. Conductivity measurements of the electrolyte and its frequency behaviour were determined by the Impedance spectroscopy. The electrolyte films measurements were carried out at room temperature in the frequency range of (40 Hz -1 MHz) using Biologic SP-150. The structural analyses of the electrolytes were examined by XPERT PRO diffractometer. The interaction between the polymer matrix and the salt was determined using FT-IR Spectrophotometer (Miracle 10 SHIMADZU). The stability of polymer electrolyte was performed by thermal analysis using Exstar – SII-TG/DTA 6300 from room temperature to 800æ%C. Roughness factor was tested by 3D Optical Profilo Meter (Zeta-20).

3. Results and Discussion

3.1 X-ray diffraction analysis

Fig.1 shows characteristic X-ray diffraction patterns of the prepared electrolytes with various concentrations encompassing two plasticizers. The pectin diffraction pattern shows a structure that is partly crystalline with a major peak at 21.7æ%C. The broad diffused bands positioned nearly about 23 to 24æ%C for the EC based electrolytes were noticed. The polymer electrolyte- SN added system exhibited broader peak than the former centred at about 25.9æ%C endorsed to the non- crystallinity of the electrolytes. Differences in the range of the peaks show that the SN based electrolytes are more effective in salt dissociation. With increase in the concentration of salts, the peaks obtained showed decrease in intensity with increase in broadness [16]. Decreased intensity shown by the featured peaks reveals the amorphousity of the polymer electrolyte. Polymer electrolytes with plasticizer assure further enhancement in amorphousity of the samples when compared to the electrolytes without plasticizers [17].

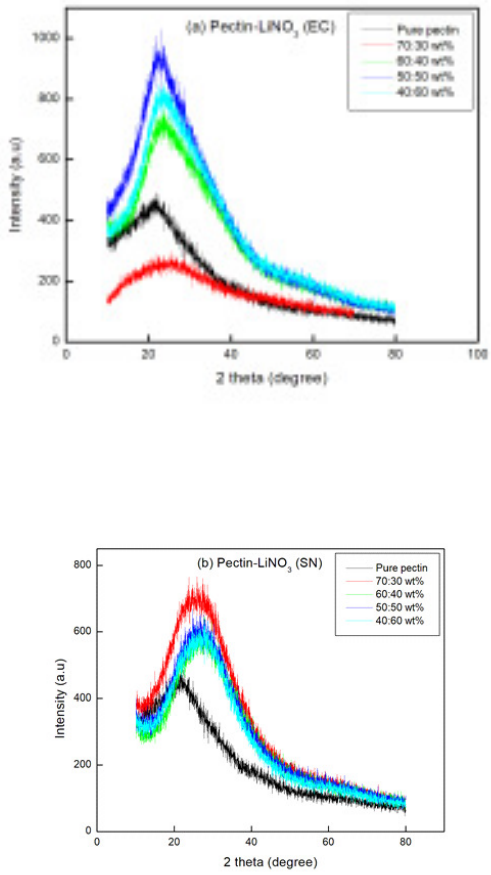
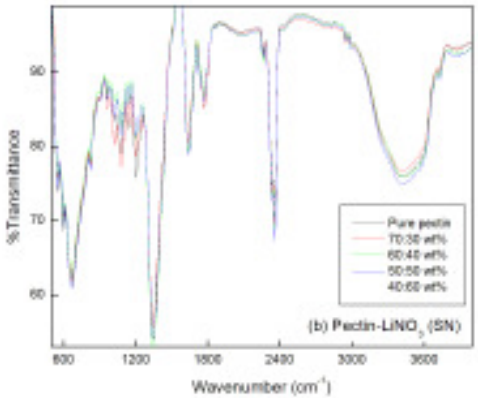


Fig.1. XRD spectra of pectin and (a). Pectin-$LiNO_3$- EC (b). Pectin- $LiNO_3$- SN polymer electrolytes.

It is also observed that the 70:30 wt. % EC based electrolyte showed an unexpected very low intensity peak broader than the pure pectin may be due to the widespread dissociation. The whole dissociation of the lithium salt in pectin polymer matrix and the complex formation is evident from the absence of peaks corresponding to the $LiNO_3$ salt.

3.2 FTIR spectroscopic analysis

Acids groups in the pectin depict an OH stretching which shows deep and very large absorption in the region of 3300–2400 cm^{-1}. The results of FT-IR study of ethylene carbonate (EC) and succinonitrile (SN) introduced electrolyte films gives relatively equivalent peak shifting (Fig. 2). The peaks obtained in the mentioned region might be due to the -OH groups and adsorbed moisture molecules of the prepared electrolyte [18]. The C–H stretching vibration in pure pectin is a weak band at 2924 cm^{-1} of CH_2 group, which is shifted to higher intensity in the doped systems. In the doped film the band corresponding to C=O stretching of $–COOCH_3$ appears at 1735 cm^{-1} is shifted to 1766 cm^{-1} and 1774 cm^{-1}. Peak at 1632 cm^{-1} attributed to the O=C–O vibrations is moved to 1635 and 1643 cm^{-1} in the electrolytes. The bands at 1365 cm^{-1} (–OH bending vibration), 1157 cm^{-1} (–CH–OH) and at 1010 cm^{-1} (–CH–O–CH–) consistent to stretching vibration of pure polymer gets increased in the Pectin-$LiNO_3$ electrolyte.



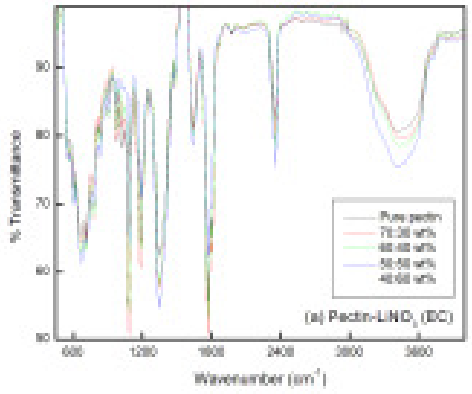
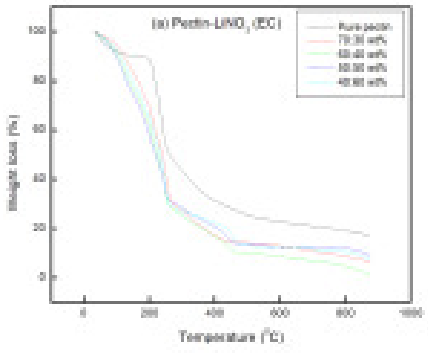


Fig.2 FTIR spectra of pectin and (a). Pectin-$LiNO_3$- EC (b). Pectin- $LiNO_3$- SN polymer electrolytes.

A band at 1735 cm^{-1} is owed to the CO stretching of $COOCH_3$ and bands 1420cm^{-1} and 1630–1640 cm^{-1} corresponds to the carboxylate ions (COO”) symmetric and asymmetric stretching vibration. The introduction of a peak nearly at 1080 cm^{-1} demonstrates the interaction of the biopolymer and the salt in the host matrix of the doped electrolyte.

3.3 Thermogravimetric analysis

The TGA measurements of the thin film samples evidence a 10% mass loss from room temperature to 120^0C, which is assigned to water loss showed in Fig.3. It is stated that lithium nitrate is a hydrophilic substance also its presence upholds a better capacity of absorbing water in the obtained film [19]. At temperatures 200–260^0C, pectin exhibited much emphasized mass loss of 40%, which indicated the decomposition, then continued deliberately until the temperature reaches 880æ%C and leaving behind 16% residue. [19].



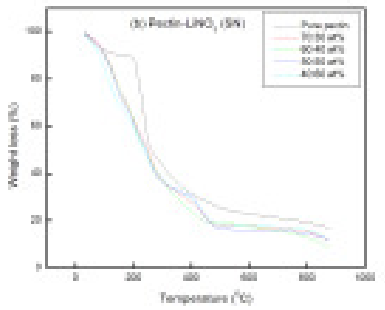
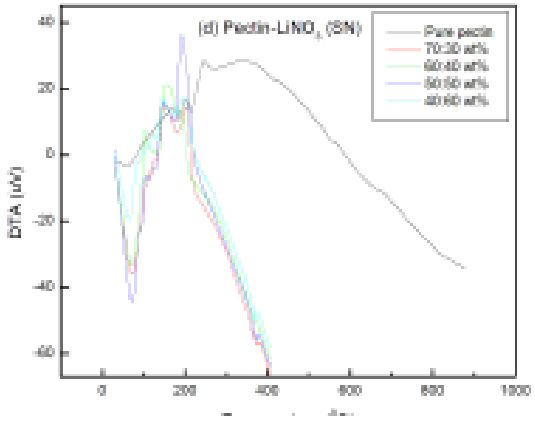


Fig.3. Thermal analysis of pectin and (a). Pectin- $LiNO_3$- EC (b). Pectin- $LiNO_3$- SN polymer electrolytes.

For samples that are conducting, the mass loss behaviour is relatively changed. The electrolyte film degradation begins at 140^0C for SN and 150^0C for EC samples and takes place majorly in other three stages, due to the lithium salt interactions with the polymer chain. Nearly 60- 75% loss of weight is observed at 240-250^0C and no significant changes were seen till 800^0C. Formerly 6–9% left over residues is may be a result of the grafted products. It is obvious that the 14% deposits conversed earlier were larger than the experimentally modified electrolytes. On comparison with the polymer, doped and plasticized samples thermal stability have been affected which supports the FTIR data witnessing the interaction of the salt and the polymer [20].



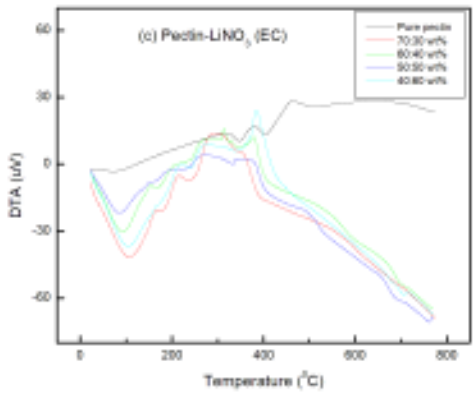


Fig. 4. DTA curves of pectin and (c). Pectin- $LiNO_3$- EC (d). Pectin- $LiNO_3$- SN polymer electrolytes.

DTA curve shows an endothermic curve between 101-104^0C. The first and second exothermic curve occurs in the range of 150-220^0C and the third curve at 250–400^0C for all the modified electrolytes. EC based samples exhibited three major exothermic curves while SN based samples resulted with two major and one minor curve. Thus the decomposition of the polymer film is found to be relative to the spotted TG results.

3.5 Electrochemical Impedance Spectroscopic analysis

An AC impedance spectrum in the low frequency series demonstrates a line and a slope, allied to the effects of diffusion of Li-ion on the interface concerning the bulk phase of the active material. In relevant with the transfer of charge analogous to electrolyte film formation, a semicircle is produced due to the rise and fall of the resistance [11]. According to the theoretical analysis, appearance of two semicircles in the impedance spectrum with higher and lower frequencies associated with the interfacial impedance and a constant phase is common [21] [22]. For plasticized polyelectrolyte films the semicircle of high frequency does not seem in practical [21]. The disappearance of semi-circular region for the samples with addition of salt [22] based on conduction of ions inferences the effect of plasticizers on the polymer chain which depends on the nature of the

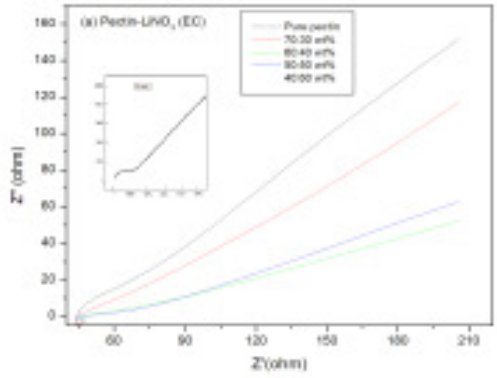


Fig. 5. Nyquist plot of pure pectin and Pectin- $LiNO_3$- EC samples

plasticizer and its interaction. The plasticizers provide more mobile ions by enhancing the conductivity behaviour of the resulted samples.

Because of the greater inductive effect persists in the samples the proper initial semicircle curve is absent which shows that the further optimization of the concentration of the plasticizer is required. The Pectin- $LiNO_3$- SN electrolyte films did not show any consistent impedance curve. Since the highest conductivity at room temperature is found to be approximately 7.5×10^{-4} S cm^{-1} for the 50: 50wt % polymer electrolyte doped with $LiNO_3$ and EC.

3.4 Morphological study

3D Laser profilometry analysis

The topography of surface and its features of polymer electrolyte films are studied using 3D-Laser Profilometer**.** The roughness of the sample with different concentrations of polymer electrolytes surface varies accordingly. The images exhibit the three dimensional surface area of the sample with the average roughness (Ra) value. The topographical representations of surface features (thickness, roughness/ smoothness) of 80:20, 70:30, 60:40 and 50:50 wt.% Pectin- $LiNO_3$ polymer electrolytes are shown in the Figures 6 and 7.

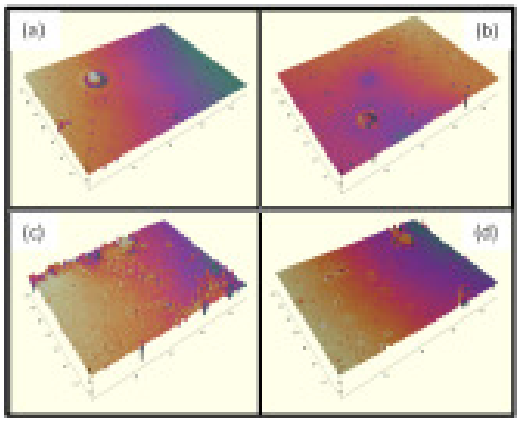


Fig.. 6. Zeta 3D images of Pectin- $LiNO_3$- EC based electrolytes (a). 70:30wt% (b). 60:40wt % (c). 50:50wt% (d). 40:60wt%

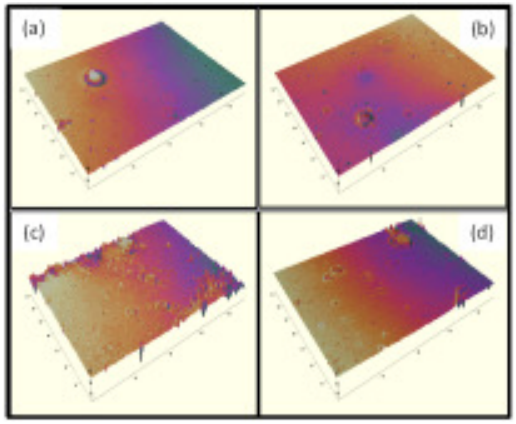


Fig. 7. Zeta 3D images of Pectin- $LiNO_3$- SN based electrolytes (a). 70:30wt% (b). 60:40wt % (c). 50:50wt% (d). 40:60wt%

The increase in the Ra value reveals the increase in the roughness of the sample. From the Ra values, it is found that among the prepared polyelectrolyte thin films, the SN based electrolyte samples show lesser Ra value of about 10- 20% than the EC based electrolytes of almost 30- 50 % due to the partial crystallinity of the EC plasticizer respectively. Thus the Pectin- $LiNO_3$- SN polyelectrolyte thin films were comparatively smoother than the Pectin- $LiNO_3$- EC electrolytes.

4. Conclusion

The effect of lithium nitrate ($LiNO_3$) salt on the biopolymer Pectin with ethylene carbonate (EC) and Succinonitrile (SN) based solid polymer

electrolytes were studied. The highest ionic conductivities attained for the EC based electrolyte film is approximately 7.5× 10-4 S cm^{-1} at 50 wt. % and 50 wt. % of the lithium salts doped. FTIR spectra validated the interaction of lithium ions with the hydroxyl groups of the polymer pectin. The ion pair formation was observed by a new peak appearance at 1080 cm^{-1} in $LiNO_3$ salt- doped systems, respectively. XRD results exhibits the amorphous nature of the films indicating the ease mobility of ions in the system. The Thermogravimetric analysis demonstrated the stability of the prepared electrolyte up to elevated temperatures. Samples morphology investigated by the 3D- Laser profilometry provides the average roughness value of the film samples. These results point out that both systems Pectin- $LiNO_3$- EC and Pectin- $LiNO_3$- SN were suitable as an electrolyte in lithium-ion battery application.

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