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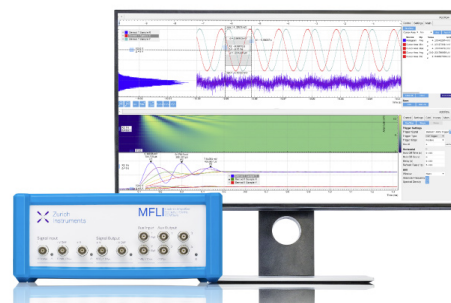
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Conductive Bio - Polymer Electrolyte with Lithium salt for Application in Electrochemical Device

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Abstract: Polymer electrolytes are the emerging materials for electrochemical device applications such as high energy density batteries, fuel cells, supercapacitors, electrochromic displays, etc. Polymer electrolytes has gone through different developmental stages, starting from dry solid polymer electrolyte (SPE) systems to plasticized, gels, rubbery to micro/nano-composite polymer electrolytes. The main two factors that retard the applications of synthetic polymer electrolytes are High cost and not “environmentally green”. Hence to overcome this shortcomings of synthetic polymers biopolymers have gained enormous attention which raises the significance due to global warming and energy crisis. The present work focuses on the characteristics of bio polymer electrolyte based on pectin and lithium nitrate. The electrolytes were prepared using the solution casting method . A.C. impedance spectroscopy shows that the biopolymer containing 30 wt% Pectin: 70wt%LiNO₃ has highest ionic conductivity of $3.97 \times 10^{-3} \text{ Scm}^{-1}$ [1]. The analysis also proves that the magnitude of ionic conductivity increases with an increase in temperature for which the activation energy is minimum. The values of glass transition temperature (T_g) using differential scanning calorimetry (DSC) analysis predicts values, which reveals that the T_g value increase with respect to the increase of LiNO₃. Transference number measurement confirms that the conducting species are Li ion. Primary lithium-ion battery has been constructed using best conducting bio polymer electrolyte membrane, and the open circuit voltage (OCV) has been observed as 1.4 V.

INTRODUCTION

Today's modern society, demand clean and sustainable energy sources to meet the growing global energy for devices and environmental challenges. Solid polymer electrolyte (SPE) plays a vital role in device application due to its various advantages such as no leakage of electrolytes, higher conductivity, high mechanical stability and good adhesive properties than liquid electrolytes. There has been plenty of research focusing on synthetic polymers for polymer electrolytes but they are non-biodegradable and toxic which can cause environmental issues[2]. One of the suitable technology to overcome this issue is to use green energy and green materials for devices. From this green point of view new biopolymer electrolytes have been developed by many researchers owing to their abundance in nature, low cost, environment friendly and potential as substitute for some petrochemicals[3]. Bio polymers such as Chitosan, starch, pectin, agar, methyl cellulose and cellulose acetate which are natural polymers have been proposed by researchers to develop SBP electrolytes. Among the different biopolymers pectin has been preferred to grow the Li-ion conducting primary battery due to its abundance in nature, less toxicity, and anionic polysaccharide found in the cell wall of apple, pomace, and oranges plants [4]. The structure of biodegradable pectin with molecular formula C₆H₁₀O₇ contains the complex mixture composed of 1,4 α -D-galacturonic acid monomer partially methyl esterified [5]. The anionic structure of pectin increases the number of coordination sites in polymeric structure which

in turn increases the ion dissociation which enhance the ionic conductivity. The mobility of the ionic carriers in the salt increases the ionic conductivity of the electrolyte membrane. In comparison with other salts lithium salts are more popular due to their properties such as light weight and higher dissociation prospects. Among various lithium salts, lithium nitrate (LiNO_3) owing to its electronegativity and delocalization of charge is of special interest [6]. Here we report the development of solid bio polymer electrolyte films of pectin added with lithium nitrate and utilized it for battery application. To our knowledge no previous report has been published on battery application of electrolyte containing pectin and lithium nitrate.

MATERIALS AND METHODS

Pectin and lithium nitrate were purchased from SRL Company Pvt Ltd, and used without further purification. The biopolymer Pectin added with different mole percent of LiNO_3 such as 60Pectin/40 LiNO_3 , 50Pectin/50 LiNO_3 , 40Pectin/60 LiNO_3 and 30Pectin/70 LiNO_3 were prepared by solution casting technique. The mixture were mixed together and stirred continuously for 24 hours until to get homogenous solution. The solution is then been cast into petri dishes and samples are vacuum dried at 50°C . These films were subjected to further characterization. The AC impedance measurements were carried out using HIOKI 3532-50 LCR HITESTER at different temperatures in the frequency range of 42 Hz to 1 MHz. The DSC thermograms have been recorded using Perkin Elmer DSC 4000 instruments. Transference number measurement was performed using dc polarization method. As the application of fixed dc voltage (1.5 V) across the sample mounted between two stainless steel electrodes the dc current is monitored as a function of time. Using the configuration $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/50\text{CA}/50\text{LiNO}_3/\text{PbO}_2 + \text{V}_2\text{O}_5$ primary lithium battery using the membrane with the highest ionic conductivity as electrolyte has been constructed. The open circuit voltage and discharge characteristics have been studied.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

Fig. 1a and b shows the XRD pattern of pure pectin and pectin doped with different molar ratios of LiNO_3 [1]. The two principal diffraction peaks at 13° and 21° reveals the semi-crystalline polymer structure of pure pectin. In the salt added system, the intensity of the peak decreases and the broadness of the peak increased, which improves the amorphous nature of the polymer membranes. This changes reveal the decrease in crystalline nature of the complexed system. This result can be interpreted in terms of the Hodge et al. [7] criterion which has established a correlation between the height of the peak and the degree of crystallinity. Further, no extra peaks corresponding to LiNO_3 in the salt added compositions evidence the complete dissolution of the salt in the polymer matrix.

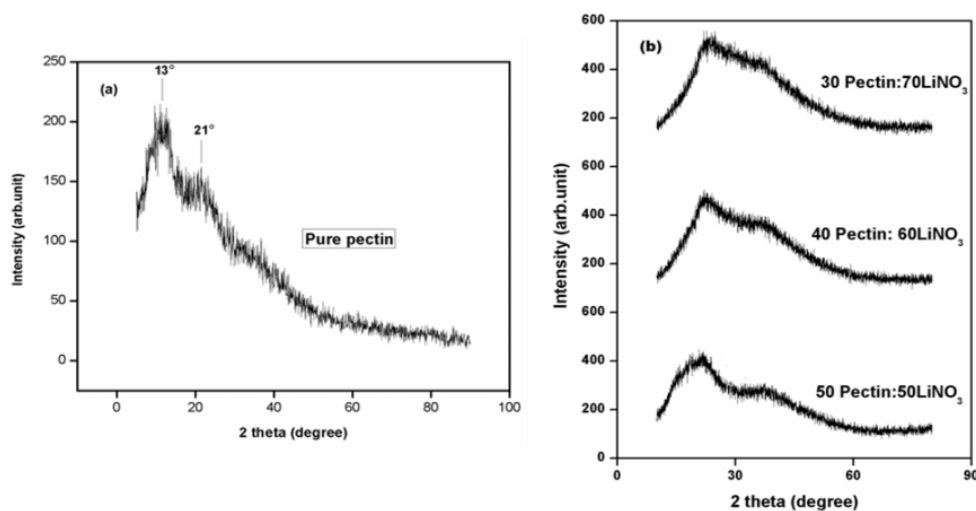


FIGURE 1. (a) XRD pattern of pure pectin (b) Pectin doped with different concentration of LiNO_3

Temperature dependent conductivity

The temperature dependent ionic conductivity nature for the complex Pectin:LiNO₃ polymer electrolyte was carried out over the temperature range 303–343 K.

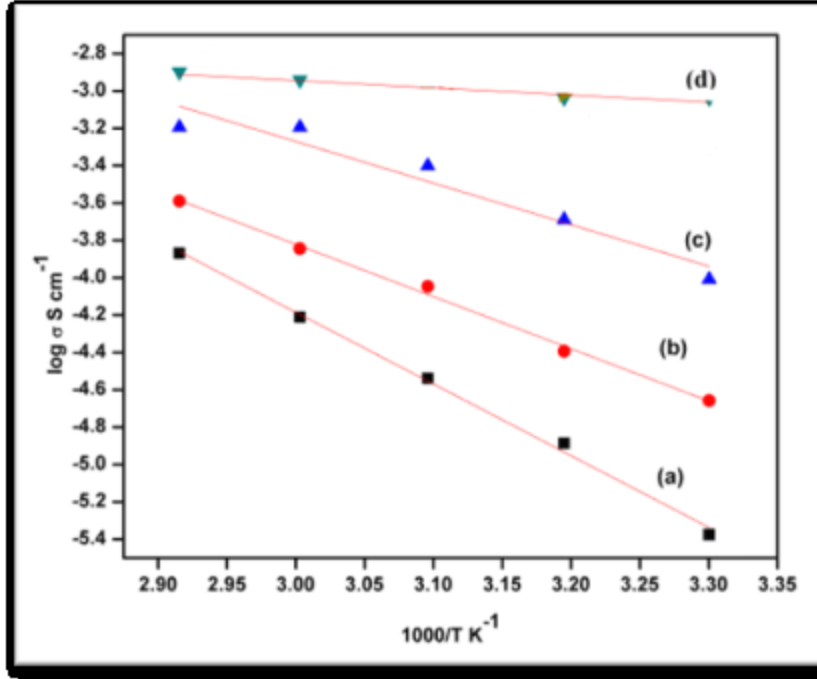


FIGURE 2. Arrhenius plot for (a)Pure Pectin (b)40Pectin:60LiNO₃ (c)30Pectin:70LiNO₃(d) 20Pectin:80LiNO₃

The variation of logarithm of electrical conductivity with inverse absolute temperature for the complex pectin:LiNO₃ polymer electrolytes that were plotted over the temperature range 303–343 K is shown in Fig. 2. Mechanism of ion transportation in polymer electrolyte can be analysed using temperature dependent parameters. The ionic conductivity value increases with increase in temperature due to the impairment of the weak bonds between oxygen atoms of pectin, and Li cations [8]. The Arrhenius theory which relates the conductivity with temperature has been stated as:

$$\sigma_T = \sigma_0 \exp\left(-\frac{E_a}{KT}\right) \quad (1)$$

where A is a constant which is proportional to the amount of charge carriers, E_a is activation energy, K is the Boltzmann constant, and T is the temperature in Kelvin (K). The activation energy (E_a) values are calculated by the linear fitting of Arrhenius plots and tabulated in table1. The maximum ionic conducting polymer film having the lowest E_a which indicates the ionic conduction is more favorable.

TABLE 1. Activation energy values for the prepared samples

Composition	Activation Energy (eV)
100Pectin	1.42
40Pectin:60LiNO ₃	0.84
30Pectin:70LiNO ₃	0.61
20Pectin:80LiNO ₃	0.75

Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of polymer electrolyte were determined using DSC analysis. The change in T_g of pure pectin due to the addition of salt (LiNO_3) is shown in the fig. 3. The glass transition temperature (T_g) of pure pectin membrane was found to be 90°C ; which is in well accordance with the previous report [9]. With the addition of salt LiNO_3 , T_g has been decreased maximum to 52.35°C for the composition 30%Pectin:70% LiNO_3 which enhances the maximum conductivity. This is due to the plasticizing effect of the salt in the host polymer matrix. Further increase in the LiNO_3 concentration as 20%Pectin:80% LiNO_3 , increases the T_g value to 67.02°C . This may be due to the effect of excess salt which reduces the flexibility of polymer chain due to the formation of ion aggregates or reduced dipole interaction of homopolymers [10]

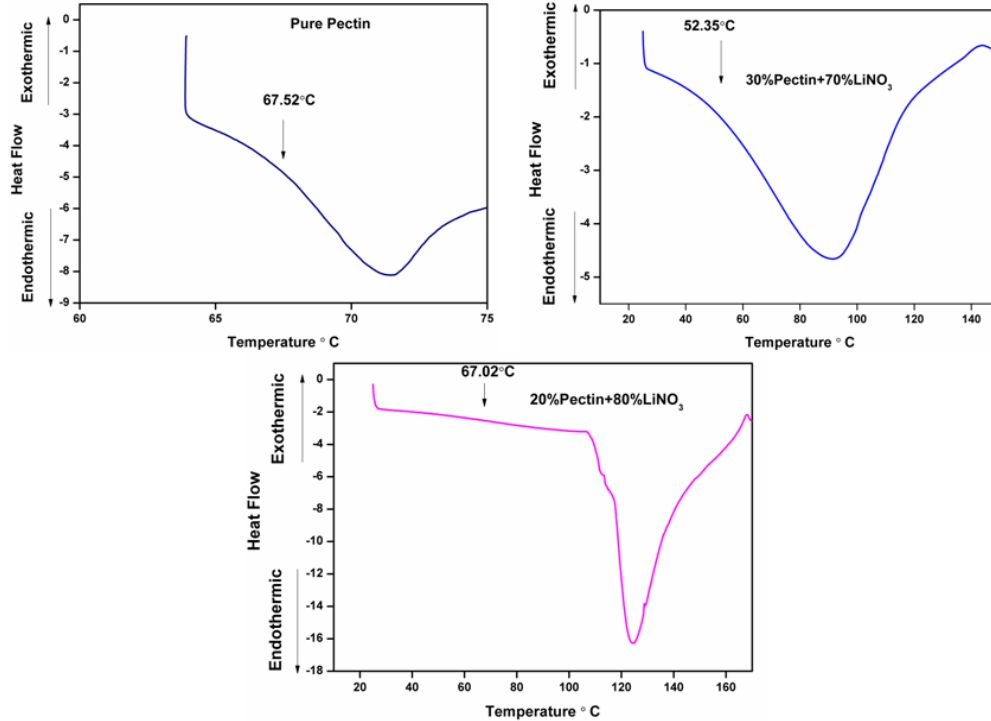


FIGURE 3. DSC thermograms for the prepared membranes

Transference Number Measurement

The ion transference or transport number indicates the contribution of different ions to total electric current in the polymer electrolyte. The transference numbers were calculated using the equation:

$$t_{ion} = \frac{I_i - I_f}{I_i} \quad (2)$$

where, I_i is the initial current and I_f is the final current

To determine the total charge transport of the polymer electrolyte film, cell with a configuration, stainless steel/30%Pectin:70% LiNO_3 /stainless steel was prepared and polarized by giving a constant dc potential of 1.5 V. The plot between polarization current versus time for 30%Pectin:70% LiNO_3 polymer electrolyte film at 303 K is shown in Fig. 4. Initially, the polarization current decreases with time, which happens when the migration of ions due to the applied field balanced by diffusion and hence leads to the cell polarization [11].

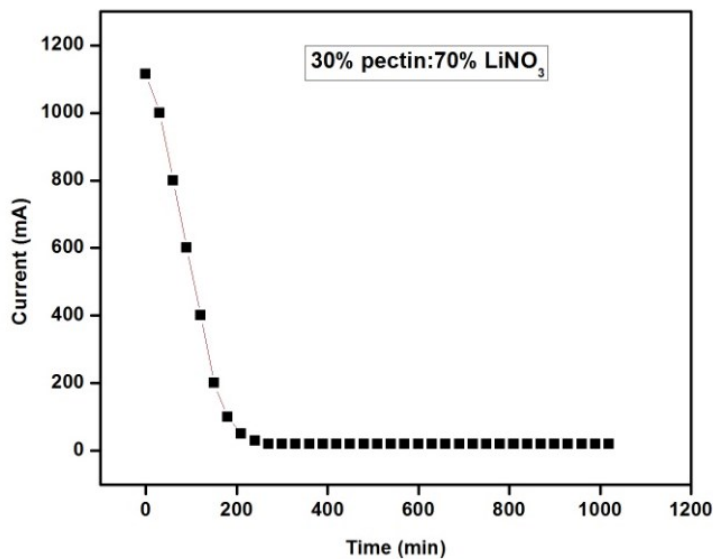


FIGURE 4. Polarisation current versus time for the maximum conducting membrane

The value of ionic transference (t_{ion}) number for the highest conducting polymer electrolyte film 30%Pectin:70%LiNO₃ is calculated as 0.99. This suggests that the charge transport in this polymer electrolyte was primarily due to ions, which are close to unity and only a negligible contribution comes from the electron.

Fabrication of Lithium ion battery

Amount of zinc powder ZnSO₄·7H₂O, and graphite powder were taken in 3:1:1 proportion, mixed together and finally ground well. The prepared mixture was pressed to form a thin anode pellet. PbO₂, V₂O₅ and graphite were taken in the ratio of 8:2:1:0.5 and polymer electrolyte were taken and mixed together and finally ground well. Then this mixture was made into thin cathode pellet. Graphite C was added to introduces the electronic conductivity, while the addition of the polymer electrolyte decreases the electrode polarization [12]. A primary lithium ion battery is constructed using maximum conducting membrane 30%Pectin:70%LiNO₃ with the configuration Zn + ZnSO₄·7H₂O/30%Pectin:70%LiNO₃ /PbO₂ + V₂O₅. The anode and cathode reactions are given below.

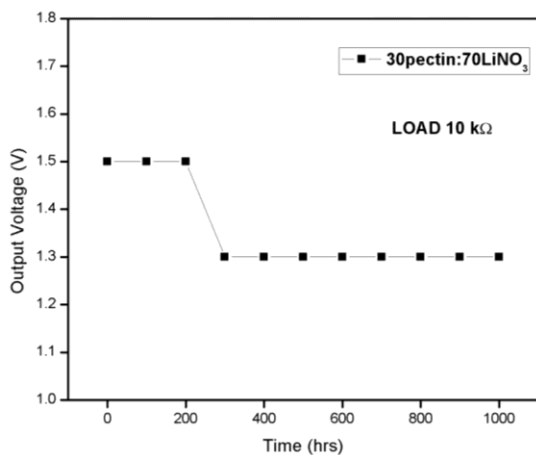
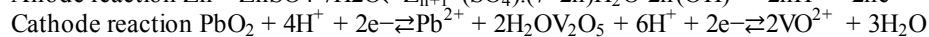
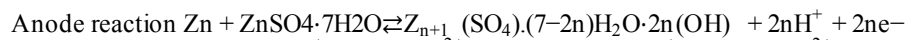


FIGURE 5.(i) Open circuit voltage with its output image

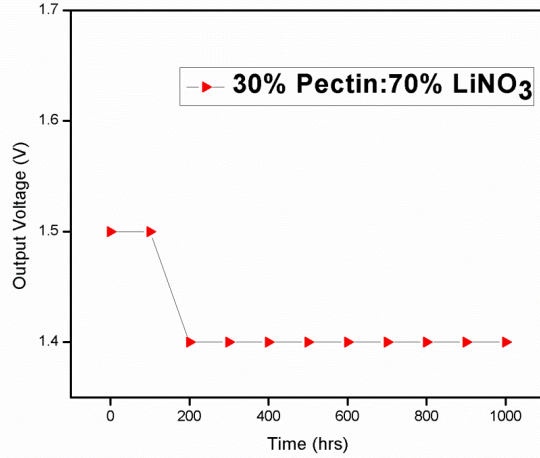


FIGURE 5.(ii) Discharge performance of the maximum conducting membrane

H^+ ions produced at the anode site repels Li^+ ions in the polymer. This process continues and the Li^+ ions by hopping mechanism reach the cathode site[13]. Fig 5(i). shows the open-circuit voltage (OCV) of constructed primary lithium ion battery, and graph has been plotted OCV versus time. The OCV of constructed primary lithium ion battery is 1.5 V and has been found to slightly reduced to 1.4V in 200 hours. The cell is allowed to equilibrate under the value of 1.4 V in open circuit condition for 1000 hours. The intermediated drop in the voltage of the cell after fabrication was due to the cell formation reaction at the electrodes.

TABLE 2. Cell Parameters

Cell Parameters	Measured values of discharge through 10k Ω
Cell Area (cm ²)	1.212
Cell weight (g)	1.15
Effective cell diameter (cm)	1
Cell thickness (cm)	0.391
OCV (V)	1.5
Discharge time for plateau region (h)	700

The stabilized voltage of 1.4 V observed in the cell was discharged through 10 k Ω load resistance at room temperature. Discharge behavior of the cell with time was shown in Fig. 4(ii), which indicates that the cell potential decreases during discharge. While discharging through 10 k Ω load, the voltage of the cell has been remains same at 1.5 V for 200 hours and drops to 1.3 V and remains constant for 1000 hours. The region in which the voltage remains constant is called as the plateau region. The OCV and discharge time for plateau region and other cell parameters for this cell were listed in Table 2. The current drawn for different resistance were tabulated in Table 3. The stabilized voltage of 1.4 V observed in the cell was discharged through 10 k Ω load resistance at room temperature. Discharge behavior of the cell with time was shown in Fig. 4(ii), which indicates that the cell potential decreases during discharge. While discharging through 10 k Ω load, the voltage of the cell has been remains same at 1.5 V for 200 hours and drops to 1.3 V and remains constant for 1000 hours. The region in which the voltage remains constant is called as the plateau region. The OCV and discharge time for plateau region and other cell parameters for this cell were listed in Table 2. The current drawn for different resistance were tabulated in Table 3.

TABLE 3. Current drawn for different resistance

Resistance Ω	Current Drawn (mA)
10K	6.84
100K	6.23
220K	5.79
370K	5.41
490K	4.87

CONCLUSION

The pectin/LiNO₃ solid biopolymer electrolytes have been prepared by solution casting technique. The conductivity of the prepared membrane gets enhanced with increase in temperature and obeys Arrhenius behaviour. The activation energy decreases with increase in temperature. Transference number measurement proves the conductivity of the polymer film is highly influenced by ions. A primary lithium ion battery has been constructed, and the open-circuit voltage and discharge characteristics have been reported.

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