Investigation of seaweed derivative iota-carrageenan based biopolymer electrolytes with lithium trifluoromethanesulfonate

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Abstract

In the present work, iota-carrageenan (i-carrageenan) biopolymer derived from edible seaweed has been chosen as the host polymer material for battery electrolyte. Ionic salt of lithium trifluoromethanesulfonate (LiCF\textsubscript{3}SO\textsubscript{3}) commonly known as lithium triflate has been added with the host polymer as a source of charge carriers. The polymer membranes of 1.0 g i-carrageenan with LiCF\textsubscript{3}SO\textsubscript{3} of various compositions (0.1 wt% to 0.5 wt%) have been prepared by solution casting technique. X-ray diffraction (XRD) results indicate the enhancement in amorphous nature of polymer membranes due to the addition of LiCF\textsubscript{3}SO\textsubscript{3}. Complex formation between the salt and polymer has been studied by Fourier Transform Infrared (FTIR) spectroscopy. The high ionic conductivity of 1.27 \times 10^{-3} \text{ S cm}^{-1} at room temperature is achieved with the combination of 1.0 g i-carrageenan : 0.4 wt% LiCF\textsubscript{3}SO\textsubscript{3} by AC impedance analysis. Total ion transference number estimated for the highest conducting sample is 0.95 by Wagner’s DC polarization method and electrochemical stability of the same is 3.52 V by Linear Sweep Voltammetry (LSV) measurement. Lithium ion conducting battery has been fabricated using the highest conducting polymer membrane. Its open circuit voltage is measured as 1.70 V and its performance is studied.

Introduction

The craving for energy storage devices from bio derived materials have been increased over the past few decades. This consciousness urges the researchers towards biopolymers over synthetic polymer for the fabrication of electrolytes in the case of solid state batteries, supercapacitors, supercapatteries, etc. Solid biopolymer electrolytes retain a prominent place in solid state batteries due to their non-toxicity, eco-efficiency, biodegradability and flexibility with good electrochemical stability [1]. Also, biopolymers overcome the shortfall of high cost of synthetic polymers. Their natural abundance and adhesive nature motivate the researchers to make use of these as efficacious material for the fabrication of solid polymer electrolyte.

Recently, seaweed derivatives gain much attention as a source of biodegradable polymer matrices. iota-carrageenan (i-carrageenan) is one such type of edible seaweed, biodegradable and water soluble polymer. This polymer exhibits excellent film forming character and this is used as a polymer host matrix in this work. Being an anionic polymer, this host matrix could provide more active coordination sites with polar groups such as hydroxyl and sulfate. These active sites could afford better ion dissociation capability with metal salts which is essential for superior ionic conductivity [2]. Conventional way of incorporating lithium salt with the polymer matrix is proved to be the easiest as well as successful method in bringing down the crystallinity as per the literature reports [3]. The salt as ionic donors enhances the concentration of ions in the polymeric system and in consequence mobilization of ions through the polymer matrix offer good ionic conductivity. Generally, it is...
propitious to have bulkier anions to curtail the mobility of anions in the polymer matrix. In this view point, ionic salt of lithium trflate (LiCF₃SO₃) salt is chosen owing to its small ionic radius of lithium and large anionic size of trflate which could lead higher ionic conductivity.

Mobarak et al have reported a conductivity value of $5.85 \times 10^{-3}$ S cm$^{-1}$ for carrageenan based electrolyte system with lithium nitrate [4]. Amran et al have studied the effect of LiCF₃SO₃ on the complexation with potato starch- chitosan blend polymer electrolytes and reported a conductivity value of $1.32 \times 10^{-3}$ S cm$^{-1}$ for the composition of 45wt% LiCF₃SO₃ and 30 wt% of glycerol [5]. Arof et al have reported a conductivity value of $6.29 \times 10^{-4}$ S cm$^{-1}$ at room temperature with a polymer salt complex prepared from chitosan, I-Carrageenan, H₃PO₄ and PEG [6].

To date, conductivity studies on i-carrageenan with lithium trflate is not available in literature. This paper describes the fabrication of low cost, light weight, flexible and new safe electrolyte system of i-carrageenan with lithium trflate. The synthesized membranes are characterized by XRD, FTIR, DSC and AC impedance analysis. AC impedance analysis confirms the conductivity value is of the order of $10^{-3}$ S cm$^{-1}$ for the highest conducting fabricated polymer membrane. Also the maximum conducting sample exhibits an excellent electrochemical stability which is ensured by linear sweep voltammetry for practical applicability.

Experimental technique

Materials and preparation of biopolymer membranes
1.0 g of i-carrageenan (Tokyo Chemical Industry, Japan) powder was dissolved in hot distilled water and magnetically stirred for an hour and lithium trflate (SRL Private ltd, Mumbai) salt of various compositions (0.1, 0.2, 0.3, 0.4 and 0.5 wt%) were incorporated with polymer solution. The mixtures were allowed to stir continuously until the attainment of homogenous solution. Then, the mixtures were transferred into the clean petri dishes and left to dry in oven. The drying process was continued until the obtainment of free standing transparent thin films.

Characterization of biopolymer electrolytes

X-Ray diffraction (XRD) analysis
Crystalline or Amorphous nature of the prepared membranes was studied by Rigaku Ultima IV, Japan diffractometer with Cu-K$_\alpha$ ($\lambda = 1.5418$ Å) radiation at a scattering angle ranging between 10$^\circ$ to 80$^\circ$.

Fourier Transform Infrared (FTIR) spectroscopy
FTIR measurement was performed by Thermo Scientific Nicolet iS10 FTIR spectrometer. IR spectra were recorded in the transmittance mode in range 4000 to 400 cm$^{-1}$ at a resolution of 1 cm$^{-1}$ at ambient temperature.

Differential Scanning Calorimetry (DSC)
DSC measurements were carried out to analyze the glass transition temperature of the samples with the aid of TA instrument DSC Q20 V24.10 Build 122. The analysis was done at a heating rate of 10 $^\circ$C min$^{-1}$ under nitrogen atmosphere over the temperature ranging from 5 to 150 $^\circ$C.

Electrochemical Impedance Spectroscopy (EIS)
Impedance measurements were carried out by HIOKI 3532–50 LCR Hi-Tester. The samples were sandwiched between stainless steel blocking electrodes and the measurements were carried over the frequency ranging between 42 Hz and 1 MHz. A plot(cole-cole) is drawn between the real part of impedance ($z'$) along $x$-axis and imaginary part of impedance ($z''$) along $y$-axis. The obtained impedance plot was then used to extract bulk resistance value by Boukmap software [7] and the ionic conductivity of the prepared samples was calculated

$$\sigma = \frac{l}{AR_b} S \text{ cm}^{-1}$$

where $l$ is the thickness of the polymer electrolyte sample and A is the contact area between the electrolyte and electrodes. $R_b$ is the bulk electrical resistance of the electrolyte obtained from the Boukamp EQ software.

Transference number measurement (TNM)
The ionic transference number of the prepared maximum conducting polymer membrane was found by Wagner’s DC polarization method by sandwiching the sample between stainless steel electrodes. A fixed DC potential of 1.5 V is applied across the sample and the DC current was monitored as a function of time. From the initial and final current values, ionic transference number of the high conducting sample was found.
Linear sweep voltammetry (LSV)
The electrochemical stability of the highest conducting prepared polymer membrane at room temperature was analyzed by LSV. The sample was scanned at a rate of 1 mV s$^{-1}$ with a linearly varying potential 0 to 5 V and the change in current is recorded.

Results and discussions

XRD
X-ray diffraction patterns of pure i-carrageenan and i-carrageenan complexed with LiCF$_3$SO$_3$ are shown in figure 1(A) and deconvoluted XRD patterns are shown in figure 1(B). Pure i-carrageenan has a characteristic peak centered at 22.1° indicating its semi crystalline nature. The sharp peaks at 31.9° and 45.7° are due to impurities [8, 9]. It is obvious from the XRD patterns that the characteristic peak becomes less prominent in the complexed membranes with the increasing concentration of LiCF$_3$SO$_3$. The characteristic peak of host polymer widens gradually with decline in peak height for the salt concentration of 0.1 to 0.4 wt% LiCF$_3$SO$_3$ with i-carrageenan. The reduction in intensity with broadness of Bragg peaks could be ascribed as the disruption of ordered phase of i-carrageenan by LiCF$_3$SO$_3$. This reveals the attainment of amorphous phase which is generally in line with the increase of carrier ions concentration. Amorphous phase accompanied by charge carrier concentration usually enhance ionic diffusivity in polymer electrolyte system [10]. The maximum amorphous nature is presented by 0.4 wt% LiCF$_3$SO$_3$ content with i-carrageenan which may experience high ionic diffusivity and yield maximum ionic conductivity. Also, it clearly exhibits the interaction between salt and the oxygen atoms of host polymer.

The percentage of crystallinity has been calculated from the area under crystalline peak over total area (Crystalline + Amorphous) under the peak for all the samples. This has been executed by deconvoluting XRD patterns and the percentage of crystallinity values are provided in table 1. In these patterns, characteristic Bragg peaks of LiCF$_3$SO$_3$ are not evidenced which conveys the complete dissolution of salt in the host matrix. But the host matrix attains saturation with the salt content of 0.4 wt% of lithium triflate and the increase in crystallinity is noticed for the salt content of 0.5 wt% of lithium triflate. This may be due to the recombination of ions.

FTIR
Figure 2 depicts the FTIR spectra of host polymer i-carrageenan and LiCF$_3$SO$_3$ complexed with i-carrageenan in transmittance mode. Polymer band frequencies vary due to the complexation and the band assignments are listed in table 2.

Pure lithium triflate shows characteristic bands at 1266 cm$^{-1}$ ($\nu_3$SO$_3$), 1033 cm$^{-1}$ ($\delta_2$SO$_3$), 1230 ($\delta_1$CF$_3$) and 1182 cm$^{-1}$ ($\delta_3$CF$_3$). The bands at 3490 and 1638 cm$^{-1}$ are also the characteristic bands of LiCF$_3$SO$_3$.  

![Figure 1. A XRD and 1 B Deconvoluted XRD patterns of (a) pure i-carrageenan, (b) 1.0 g i-carrageenan: 0.1 wt% LiCF$_3$SO$_3$, (c) 1.0 g i-carrageenan: 0.2 wt% LiCF$_3$SO$_3$, (d) 1.0 g i-carrageenan: 0.3 wt% LiCF$_3$SO$_3$, (e) 1.0 g i-carrageenan: 0.4 wt% LiCF$_3$SO$_3$ and (f) 1.0 g i-carrageenan: 0.5 wt% LiCF$_3$SO$_3$.](image-url)
The characteristic bands of pure i-carrageenan are at 3380, 1635, 1219, 1155, 1068, 1026, 928, 848 and 803 cm$^{-1}$ [13, 14]. The broad O–H absorption hydroxyl band at 3380 cm$^{-1}$ of pure i-carrageenan has been shifted and positioned at 3399, 3417, 3418, 3419, 3410 cm$^{-1}$ in the salt complexes 0.1, 0.2, 0.3, 0.4 and 0.5 wt % respectively due to the interaction of polymer with the salt. The H–O–H deformation band of host polymer at 1635 cm$^{-1}$ is shifted to 1639, 1639, 1639, 1641, 1636 cm$^{-1}$ in the samples of i-carrageenan with LiCF$_3$SO$_3$ of 0.1 to 0.5 wt % respectively.

The absorption band at 1219 cm$^{-1}$ (O=S=O, ester sulfate group) of host polymer gets splitted into two peaks and they are positioned at 1256 and 1227 cm$^{-1}$ in all the complexed samples due to the interaction of lithium triflate with i-carrageenan. This can be interpreted as the asymmetric SO$_3$ band of pure LiCF$_3$SO$_3$ is established in the complexed samples and ester sulfate band of i-carrageenan at 1219 cm$^{-1}$ has been shifted to 1227 cm$^{-1}$ in the salt incorporated samples.

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The shift in the Galactose position of pure i-carrageenan at 928 cm$^{-1}$ to 918 cm$^{-1}$ in salt complexes exemplifies very well the interaction of salt with the polymer. No shift is observed in 803 and 848 cm$^{-1}$ related to –O–SO$_3$ stretching vibration of D-galactose-2-sulfate and D-galactose-4-sulfate of pure i-carrageenan respectively.

FTIR analysis predicts some overlapping, band splitting and band shifts in polymer salt complex samples. This justifies the interaction of salt with the polymer and the variation of ionic conductivity value with salt composition.

**Table 1.** Percentage of crystallinity by XRD, $T_g$ and $T_m$ from DSC.

| Composition                        | Percentage of crystallinity by XRD | $T_g$ (°C) | $T_m$ (°C) |
|-----------------------------------|-----------------------------------|------------|------------|
| Pure i-carrageenan                | 31.00                             | 51.0       | 90.8       |
| 1.0 g i-carrageenan: 0.1 wt % LiCF$_3$SO$_3$ | 28.62                             | 49.3       | 86.9       |
| 1.0 g i-carrageenan: 0.2 wt % LiCF$_3$SO$_3$ | 25.44                             | 48.5       | 85.6       |
| 1.0 g i-carrageenan: 0.3 wt % LiCF$_3$SO$_3$ | 23.93                             | 47.3       | 83.8       |
| 1.0 g i-carrageenan: 0.4 wt % LiCF$_3$SO$_3$ | 20.34                             | 43.0       | 82.2       |
| 1.0 g i-carrageenan: 0.5 wt % LiCF$_3$SO$_3$ | 22.46                             | 58.2       | 93.5       |

[11, 12]. The characteristic bands of pure i-carrageenan are at 3380, 1635, 1219, 1155, 1068, 1026, 928, 848 and 803 cm$^{-1}$ [13, 14].
Table 2. FTIR band assignments of pure i-carrageenan and i-carrageenan complexed samples.

| Wavenumber (cm⁻¹) | Pure i-carrageenan | i-carrageenan : 0.1wt % | i-carrageenan : 0.2wt % | i-carrageenan : 0.3wt % | i-carrageenan : 0.4 wt % | i-carrageenan : 0.5 wt % | Assignments |
|-------------------|-------------------|------------------------|------------------------|------------------------|------------------------|------------------------|--------------|
| 3380              | 3399              | 3417                   | 3418                   | 3419                   | 3410                   |                        | O–H stretching |
| 1635              | 1639              | 1639                   | 1639                   | 1641                   | 1636                   |                        | water deformation band |
| 1219              | 1227              | 1227                   | 1227                   | 1227                   | 1227                   |                        | Ester sulphate O = S = O symmetric vibration |
| ---                | 1256              | 1256                   | 1256                   | 1256                   | 1256                   |                        | Asymmetric SO₃ vibration of LiCF₃SO₃ |
| 1155              | 1177              | 1177                   | 1178                   | 1181                   | 1178                   |                        | C–O stretching of i-carrageenan and Characteristic band of LiCF₃SO₃ |
| 1068              | 1068              | 1068                   | 1068                   | 1068                   | 1068                   |                        | C–O stretching |
| 1026              | 1032              | 1032                   | 1032                   | 1032                   | 1032                   |                        | CH₂ symmetric stretching of i-carrageenan and Symmetric SO₃ vibration of LiCF₃SO₃ |
| 928               | 918               | 918                    | 918                    | 918                    | 918                    |                        | C–O–C of 3, 6 anhydrogalactose |
| 848               | 848               | 848                    | 848                    | 848                    | 848                    |                        | – O–SO₃ stretching at D-galactose-4-sulfate |
| 803               | 803               | 803                    | 803                    | 803                    | 803                    |                        | – O–SO₃ stretching at D-galactose-2-sulfate |
In order to examine the effect of LiCF$_3$SO$_3$ on thermal transition of i-carrageenan, thermograms by DSC technique have been analysed. Typical DSC plots of host polymer and LiCF$_3$SO$_3$ complexed polymer membranes are depicted in figure 3.

The DSC plot of host i-carrageenan shows an endothermic peak at 90.8°C and a T$_g$ value of the same is 51°C. It is evident that endothermic peak broadens and the glass transition temperature (T$_g$) of the prepared complexes decrease with LiCF$_3$SO$_3$ content up to the concentration of 0.4 wt%. The value of T$_g$ decreases to 43°C for the maximum conducting polymer membrane and the melting temperature decreases to 82.2°C. The T$_g$ and T$_m$ values of all the prepared complexes along with host polymer is tabulated in table 1.

This reduction in T$_g$ may be due to the disturbance in the polymer chain by the incorporation of salt. In the present investigation, polymer matrix is disturbed by Li$^+$ ions due to the interaction with oxygen atom, which in turn enables flexibility in the polymer matrix. In general flexible polymer backbone supports easy transportation of ions which may supplement good ionic conductivity. Also, variation in T$_m$ reflects the changes in crystallinity and confirms the interaction between the host polymer and salt has changed the dynamics of polymer chain [16]. In this regard, sample with low glass temperature is expected to possess more amorphous nature to yield good conductivity value. The sample 0.5 wt% LiCF$_3$SO$_3$ with i-carrageenan shows deviation from the trend which attributes excess content of salt in the polymer matrix beyond threshold. DSC results are consistent with XRD results.

**AC impedance analysis**

Samples of i-carrageenan with different lithium triflate concentration have been subjected to the ionic conductivity measurements and the corresponding Nyquist plot of all the samples is shown in figure 4. The ionic conductivity of the samples are calculated by

$$\sigma = \frac{l}{AR_0} \text{ S cm}^{-1}$$

where $l$ is the thickness of the polymer electrolyte sample and $A$ is the contact area between the electrolyte and electrodes. $R_0$ is the bulk electrical resistance of the electrolyte obtained from the Boukamp EQ software and the equivalent circuit model is provided in figure 4.

Ionic conductivity of the pure polymer electrolyte is in the order of $10^{-5}$ S cm$^{-1}$ [9]. Ionic conductivity is found to be in ascending trend with lithium triflate up to the concentration of 0.4 wt% with the shift of impedance plot to low resistance side on the real axis. The combination 1.0 g i-carrageenan: 0.4 wt% LiCF$_3$SO$_3$ displays good ionic conductivity value of $1.27 \times 10^{-3}$ S cm$^{-1}$ at ambient temperature. Addition of salt significantly increases ionic conductivity of i-carrageenan biopolymer electrolytes by two orders of magnitude.
due to the attainment of increasing amorphous phase. DSC results suggest this high conducting sample composition possesses low $T_g$ value which implies softening nature of polymer membrane and this rubbery amorphous phase provides a favourable pathway for the transportation of lithium ions by deducing ion interaction. According to Aziz et al. folded polymer chains which are analogous to cylindrical tunnels generate channels for the transportation of cations. This demonstrates the movement of cations transportation between neighboring coordinate sites in the polymer host matrix \[17\]. Further addition of lithium triflate (0.5 wt\% of LiCF$_3$SO$_3$) has decremented the conductivity value due to the reassociation of ions to form neutral ion pairs back \[18\] and hence clearly it depicts polymer matrix attains saturation with 0.4 wt\% of LiCF$_3$SO$_3$. It is evident that 0.4 wt\% of LiCF$_3$SO$_3$ is the appropriate quantity which utters highest ionic conductivity by bringing more amorphization in the polymer membrane. As ionic conductivity is dependent on the number of charge carriers and their mobility, the effect of adding lithium triflate has made prominent changes in these factors and enriched the ionic conductivity value of biopolymer electrolytes. The calculated ionic conductivity values are presented in table 3.

Frequency dependence of conductivity is demonstrated by conductance spectra and it is shown in figure 5. It consists of low frequency dispersion and mid frequency plateau region. The low frequency dispersion region is attributed to the space charge polarization at the blocking electrodes and the mid frequency plateau region where conductivity is independent of frequency can be attributed as conductive path way for ionic movement \[13\]. The extrapolation of this independent plateau region to the $y$-axis (log $\sigma$), provides dc conductivity of the samples. Ionic conductivity values calculated from conductance spectra agree very well with the values calculated from cole-cole plot. Ionic conductivity value of the highest conducting membrane is compared with the other biopolymer electrolytes \[19–22\] with the same salt (LiCF$_3$SO$_3$) and is provided in the table 4. Ionic conductivity of the polymer membrane in the present work is high compared to other biopolymer electrolytes due to its low glass transition temperature ($43 \degree$C) and more amorphous nature as confirmed by XRD results.

Temperature dependent conductivity

The temperature dependence of ionic conductivity plot exemplifies the linear relation between the ionic conductivity and temperature. This thermal activated ion conduction process of biopolymer electrolytes suggests Arrhenius behavior of the samples. It is believed that ionic conductivity increases with amorphous nature. The amorphous phase progressively swells with temperature due to faster polymer chain segmental motion. Increase in conductivity can be attributed as the result of inter and intra chain hopping of ions. The Arrhenius relation can be expressed by

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

Figure 6 illustrates the dependence of ionic conductivity with temperature in the temperature range 303 to 373 K. The activation energy of the prepared samples is calculated from the linear fit of the Arrhenius plots and is listed in table 3. Regression values of all samples are near to unity and $E_a$ values vary from 0.19 to 0.28. The Activation energy is found to be decreasing gradually with increasing LiCF$_3$SO$_3$ salt content and it is very low for the highly conducting sample. This low $E_a$ implies faster segmental motion and free volume which favours rapid
Table 3. Ionic conductivity and Activation energy values of prepared samples at different temperatures.

| Polymer composition | Conductivity σ (S cm\(^{-1}\)) | Activation energy (eV) |
|---------------------|----------------------------------|------------------------|
|                     | 303 K | 313 K | 323 K | 333 K | 343 K | 353 K | 363 K | 373 K |                  |
| 1.0 g i-carrageenan : 0.1 wt% LiCF\(_3\)SO\(_3\) | 7.26 × 10\(^{-3}\) | 8.24 × 10\(^{-3}\) | 1.12 × 10\(^{-4}\) | 1.62 × 10\(^{-4}\) | 2.38 × 10\(^{-4}\) | 3.39 × 10\(^{-4}\) | 4.21 × 10\(^{-4}\) | 5.72 × 10\(^{-4}\) | 0.28 |
| 1.0 g i-carrageenan : 0.2 wt% LiCF\(_3\)SO\(_3\) | 1.28 × 10\(^{-4}\) | 1.73 × 10\(^{-4}\) | 2.95 × 10\(^{-4}\) | 3.71 × 10\(^{-4}\) | 4.79 × 10\(^{-4}\) | 6.16 × 10\(^{-4}\) | 7.24 × 10\(^{-4}\) | 8.12 × 10\(^{-4}\) | 0.26 |
| 1.0 g i-carrageenan : 0.3 wt% LiCF\(_3\)SO\(_3\) | 6.79 × 10\(^{-4}\) | 7.04 × 10\(^{-4}\) | 9.54 × 10\(^{-4}\) | 1.04 × 10\(^{-3}\) | 1.73 × 10\(^{-3}\) | 2.29 × 10\(^{-3}\) | 2.63 × 10\(^{-3}\) | 3.38 × 10\(^{-3}\) | 0.24 |
| 1.0 g i-carrageenan : 0.4 wt% LiCF\(_3\)SO\(_3\) | 1.27 × 10\(^{-3}\) | 1.88 × 10\(^{-3}\) | 2.19 × 10\(^{-3}\) | 2.98 × 10\(^{-3}\) | 3.04 × 10\(^{-3}\) | 3.86 × 10\(^{-3}\) | 4.42 × 10\(^{-3}\) | 5.94 × 10\(^{-3}\) | 0.19 |
| 1.0 g i-carrageenan : 0.5 wt% LiCF\(_3\)SO\(_3\) | 8.71 × 10\(^{-4}\) | 9.33 × 10\(^{-4}\) | 1.20 × 10\(^{-3}\) | 1.51 × 10\(^{-3}\) | 2.03 × 10\(^{-3}\) | 2.89 × 10\(^{-3}\) | 3.12 × 10\(^{-3}\) | 4.46 × 10\(^{-3}\) | 0.23 |
mobilization of ions [23]. It is desirable to have low activation energy for the polymer electrolyte for efficient application in electrochemical devices and also low $E_a$ implies the establishment of amorphous nature in the polymer membrane [24].
Dielectric spectra analysis

Real part of dielectric permittivity known as dielectric constant ($\varepsilon'$) and imaginary part of dielectric permittivity known as dielectric loss ($\varepsilon''$) are observed over the frequency range 42 Hz to 1 MHz at room temperature. Figures 7 (A) and (B) depicts the variation of $\varepsilon'$ and $\varepsilon''$ with frequency for pure i-carrageenan as well as i-carrageenan with different amounts of LiCF$_3$SO$_3$.

In this analysis, the obtained spectra are divided into two regions, such as low frequency and high frequency region. At low frequency, $\varepsilon'$ and $\varepsilon''$ values are high which represent the effect of electrode polarization and this high $\varepsilon'$ and $\varepsilon''$ values attribute the increased number of charge carriers density accumulation at the boundary interface. In low frequency region, the field reversal is slow, so that ions acquire enough time to keep up with the field. In the high frequency region, both $\varepsilon'$ and $\varepsilon''$ are very low and almost constant which implies the disappearance of orientation polarisation. Since, the electric field change is fast, charge carriers will not be able to keep in line with the field. Hence polarisation of a material decreases at the interface, both $\varepsilon'$ and $\varepsilon''$ decreases [25].

It is clear that, $\varepsilon'$ and $\varepsilon''$ values at different frequencies increase with increasing composition of LiCF$_3$SO$_3$.

Transference number measurement (TNM)

Wagner’s polarization technique

This is one of the most effective as well as simple technique to evaluate the contribution of ions to the total conductivity. The transference number of ions [23] at room temperature is evaluated by
where $I_i$ is the initial current and $I_f$ is the final current. The maximum conducting sample is sandwiched between the stainless steel (SS) electrodes. A small DC voltage is applied across the cell configuration of SS | 1.0g i-carrageenan: 0.4 wt% LiCF$_3$SO$_3$ (Electrolyte) | SS for polarization. The current starts to flow due to the migration of ions and the same is noted as initial current ($I_i$) and the initial current starts to decrease with polarizing time due to the exhaustion of ions. The constant current persists at last is noted as final current ($I_f$).

With these values, the transference number of ions for the maximum conducting polymer membrane is calculated and its value is 0.95 at room temperature. The transference number value indicates the ionic contribution is predominant over electronic contribution to the total conductivity value. This concludes the prepared biopolymer electrolytes are ionic conductors.

**Linear sweep voltammetry**

Figure 8 depicts the LSV plot of maximum conducting membrane i-carrageenan: 0.4 wt% LiCF$_3$SO$_3$. The linear voltage is swept to the working electrode from 0 V towards positive and simultaneously the current flowing in the circuit is observed. The anodic current starts to flow at a potential of 3.52 V. This anodic current is observed to be increasing with the applied voltage which attributes the decomposition of the polymer electrolyte. The fabricated polymer electrolyte is stable up to 3.52 V which exhibits its suitability for practical applications.

**Fabrication of Li-ion conducting battery**

To check the potential of fabricated biopolymer electrolyte, lithium ion conducting battery is constructed. ZnSO$_4.7$H$_2$O and graphite powder is taken for the anode material in a suitable ratio of 3:1:1. This mixture is grinded well and is made in the form of a thin pellet. Similarly, cathode pellet is prepared by PbO$_2$, V$_2$O$_5$, graphite and the prepared maximum conducting polymer electrolyte membrane. The fabricated maximum conducting polymer membrane (1.0 g i-carrageenan: 0.4 wt% LiCF$_3$SO$_3$) is sandwiched between anode and cathode pellets. The reactions taking place in the anode and cathode are

The anode reaction is given as follows:

$$n \text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Zn}_{n+1} (\text{SO}_4) \cdot (7 - 2n)\text{H}_2\text{O}, 2n(\text{OH}) + 2n\text{H}^+ + 2n\text{e}^-$$

The cathode reaction is given as follows:

$$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$$

$$\text{V}_2\text{O}_5 + 6\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{VO}^{2+} + 3\text{H}_2\text{O}$$

In the anode site H$^+$ ions are produced which repel Li$^+$ ions in the polymer matrix. By the process of hopping mechanism, Li$^+$ ions reach the cathode site. The same anode and cathode material for Li$^+$ conduction has been used for electrochemical testing and reported by Kingslin *et al* Sampath Kumar *et al* and Perumal *et al* [26–30].
Cell performance
The open circuit voltage of 1.70 V and a short circuit current of 1.36 mA are measured for the cell assembly and the OCV is observed for 90 h and it remains stable during the observation period. While discharging through the load of 100 KΩ, the voltage drops to 1.65 V and it remains constant for the observation period of 75 h. This stabilized voltage region is known as plateau region. The cell parameters of the study are presented in the table 5.

| Cell parameters | Measured values for 1.0g i-carrageenan: 0.4 wt% LiCF3SO3 Electrolyte system |
|-----------------|--------------------------------------------------------------------------------|
| Open circuit voltage (OCV) | 1.70 V |
| Short circuit current | 1.36 mA |
| Cell weight (g) | 1.120 g |
| Effective area of cell (cm²) | 0.829 |
| Load | 100 KΩ |
| Time for plateau region (h) | 75 h |
| Power density | 2.06 W kg⁻¹ |
| Energy density | 154.82 Wh kg⁻¹ |

Conclusion
Biopolymer membranes of i-carrageenan with various compositions of LiCF3SO3 have been developed using the solvent casting technique. A highest ionic conductivity of $1.27 \times 10^{-3}$ S cm⁻¹ at room temperature is attained by the sample composition of 1.0 g i-carrageenan: 0.4 wt% LiCF3SO3. The amorphous nature of the polymer membranes have been confirmed by XRD. The complexation of salt and polymer has been studied by FTIR. The flexibility of the polymer membrane is confirmed by its low $T_g$ value from DSC thermogram. The highest conducting polymer membrane exhibits good electrochemical stability value (3.52 V). Lithium ion conducting battery has been fabricated using the highest conducting polymer membrane (1.0 g i-carrageenan: 0.4 wt% LiCF3SO3) and the open circuit voltage is 1.70 V.

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Conflict of interest
Authors have no conflict of interest.

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