#### **ORIGINAL PAPER**



# Preparation and characterisation of chitosan extracted from shrimp shell (*Penaeus monodon*) and chitosan-based blended solid polymer electrolyte for lithium-ion batteries

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Received: 1 April 2020 / Revised: 20 September 2020 / Accepted: 6 November 2020 © Springer-Verlag GmbH Germany, part of Springer Nature 2021

### Abstract

A bioactive and non-toxic biopolymer-based electrolyte has gained attention in recent research for their potential applications in the fabrication of electrochemical devices. In this work, we extracted the chitosan successfully prepared from shrimp shells using Brine's method. The solid polymer electrolyte comprising the blend of chitosan and agar-agar, plasticised with polyethylene glycol (PEG), as host polymer and lithium perchlorate (LiClO<sub>4</sub>) as a dopant is prepared by solution casting technique. Also, the effect of different weight percentage of the plasticiser PEG at a fixed ratio of perchlorate content is investigated. The obtained chitosan blended film is highly suitable as a electrolyte for electrochemical devices. The prepared polymer electrolyte is characterised using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), high-resolution scanning electron microscopy (HR-SEM), X-ray diffraction (XRD) and electrochemical impedance spectroscopy. The ATR-FTIR spectroscopy confirms the presence of particular functional groups present in chitosan and complex formation between blended polymers and lithium perchlorate. The surface morphology and amorphous crystallinity of chitosan and blended polymer electrolytes revealed from HR-SEM and XRD analysis. The ionic conductivity of the prepared materials is studied using AC impedance spectroscopy and compared. The highest ionic conductivity at room temperature obtained for the sample is  $4.56 \times 10^{-4}$  Scm<sup>-1</sup> (CAP<sub>3</sub>). The mechanical properties of films have been studied using a Universal testing machine analysis. Wagner's polarisation measurements have estimated the Li<sup>+</sup> transport numbers of SPEs. Linear sweep voltammetry was performed on half-cell method to study the electrochemical stability window of the maximum ionic conductivity of SPEs.

**Keywords** Solid polymer electrolytes (SPEs)  $\cdot$  Electrochemical devices  $\cdot$  Solution casting  $\cdot$  Ionic conductivity  $\cdot$  Plasticiser

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#### Introduction

Chitosan is a linear polysaccharide of natural polymer essentially composed by  $\beta$ -(1,4)-linked glucosamine units (2-amino-2-deoxy- $\beta$ -d-glucopyranose) together with some proportion of *N*-acetylglucosamine units (2-acetamino-2-deoxy- $\beta$ -d-glucopyranose). It is present in green algae cell walls of fungi such as aspergillus, mucor, the cuticles of insects and arachnids and the exoskeleton of crustaceans cosmetics. Chitosan has an excellent candidate for the medicine [1], pharmacy [2], agriculture [3], food industry, wastewater treatment [4] and many other industrial applications because it can be prepared in films, fibres and micro. Chitosan is a weak base and is insoluble in organic solvent and water, but it is soluble in dilute acidic solutions of many organic and inorganic acids (pH < 6.5) due to the protonation of its amino (R–NH<sub>3</sub><sup>+</sup>) groups.

Recently chitosan-based blend solid polymer electrolytes (BSPEs), which comprise a polymer matrix and lithium salt, are used in the modern electrochemical devices because of their flexibility, electrochemical stability, dimensional stability, safety and long life span. The most challenging and critical issue for SPEs is to improve its ionic conductivity to approach the level of liquid electrolytes. Methods such as polymer blending [5], plasticisation [6], copolymerisation [7] and the addition of nanofillers [8] into polymer materials have been used to improve the ionic conductivity of solid polymer electrolyte systems. For the past decades, gel polymers electrolyte is studied with (GPEs) with non-biodegradable polymers, such as poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF) and, most recently, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [9]. Since they are not eco-friendly, which results in the generation of environmental waste, hence the researchers have focused their attention on eco-friendly biodegradable solid-state polymer electrolyte materials, for electrochemical devices.

These reported materials have several advantages, such as abundancy, environment-friendly, non-toxic, biodegradable, biocompatible, and they possess excellent film-forming properties. Among the biopolymers, chitosan, corn starch and carrageenan, agar-agar, chitosan and methylcellulose-based polymer electrolytes have been reported the highest ionic conductivity at room temperature [10–14]. Polymer blends have gained commercial importance over homopolymers and copolymers due to low-cost, simplicity of preparation and easy control of the physical properties by compositional change. Thus polymer blends are the most promising and feasible approach to improve the ionic conductivity of polymer electrolyte [14]. According to the literature, only a few numbers of investigations were carried out by employing chitosan-based blended polymer electrolyte. Salman and Omed [15] have reported a conductivity value of  $3.74 \times 10^{-6}$  Scm<sup>-1</sup> for chitosan-methylcellulose-LiBF<sub>4</sub> polymer electrolyte Sudhakar and Sivakumar [16]. The maximum conductivity is found to be  $3.7 \times 10^{-4}$  Scm<sup>-1</sup> at room temperature for chitosan/starch with LiClO4, Sunil et al. [17]. The highest ionic conductivity of  $3 \times 10^{-6}$  Scm<sup>-1</sup> at room temperature is observed for chitosan-poly (vinyl alcohol) with  $LiClO_4$  (Scheme 1).

Considering eco-friendly and pollution-free materials, the prospective use of biodegradable polymer is a lithium-ion conducting matrix that has been



Scheme 1 Chemical structure of chitosan

investigated in this study. To the best of our knowledge, no work has been done chitosan, agar–agar plasticised with PEG blend polymer doped with  $\text{LiClO}_4$  in biopolymer electrolytes for electrochemical device application. This study presents the result of such investigations on the mechanical, thermal and electrical properties of prepared biopolymer electrolytes. Thus, keeping the chitosan and agar–agar as the same weight percentage and plasticiser are the different varied composition of polyethylene glycol (PEG) solid polymer electrolyte that was prepared. The prepared blend solid-state electrolytes were characterised by a different technique such as X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), AC impedance analysis, scanning electron microscopy (HRSEM) with EDX, mechanical properties (UTM), transference number measurement (TNM), electrochemical stability analysis.

# Experimental

### **Materials and methods**

Agar–agar (SQ. 98% purity), PEG (SRL MW=600) average molecular weight 600, lithium perchlorate were purchased from Sigma-Aldrich. NaOH, HCl of industrial grade bought from the local market.

### Extraction of chitosan from (Penaeus monodon shell)

Chitosan is easily obtained from sea sources such as lobsters, crabs and shrimp, and many other organisms, including insects and fungi, especially Dungeness crab (Cancer magister), back tiger shrimp (*Penaeus monodon*), lobster or crawfish shells. These are the most abundant source of chitin and the significant sources of crustaceans that are processed into chitin and chitosan. It is one of the most abundant biodegradable materials in the world. The used raw black tiger shrimp shell (*P. monodon shell*) for the extraction of chitosan was collected from the coastal area in the Bay of Bengal Sea, Chennai Province (India). The samples were first washed with

tap water and distilled water and then dried at 80 °C for 24 h. Finally, this dried biomass was ground into small pieces (Scheme 2).

### Preparation of solid polymer electrolyte (SPEs)

The SPEs films were prepared by solution casting technique. The blend polymer is made by mixing chitosan, agar–agar and different weight percentages of (x wt%) plasticiser (PEG) with LiClO<sub>4</sub> salt. The amount of LiClO<sub>4</sub> is added as a constant 10 weight percentage. Chitosan was dissolved in 1 M acetic acid by stirring at room temperature for 1 h to obtain a transparent solution. Then agar–agar was dissolved in 50 mL double de-ionised hot water and heated at 50 °C–70 °C for 20 min with stirring; both solutions mixed continuously stirring by using a magnetic stirrer for 2 h to obtain a homogeneous solution. Then the corresponding amount PEG and LiClO<sub>4</sub> dissolved in the above solution, the solution stirring at 7 h. The clear homogeneous solution was cast in a transparent Teflon Petri dish and then evaporated at 70 °C for 8 h in the hot oven; free-standing films were obtained (Scheme 3).

# **Results and discussion**

### Fourier transform infrared spectroscopy (FTIR)

The characteristic FTIR absorption spectrum of the prepared chitosan and chitosanbased blended solid polymer electrolytes and films were recorded with Bruker ATR–FTIR spectrometer spectrum. Figure 1 represents the combined spectra for the prepared chitosan and chitosan-based blended SPEs systems.



Scheme 2 Schematic representation of the processes to prepare chitosan from shrimp shell



Polymer electrolyte

Scheme 3 Schematic representation of the preparation of polymer electrolytes



Fig. 1 FTIR spectra of prepared chitosan: a CS and b CAP<sub>1</sub>, c CAP<sub>2</sub>, d CAP<sub>3</sub>, e CAP<sub>4</sub> polymer blended electrolytes

The structure of chitosan, extracted from shrimp shell, was analysed using FTIR spectroscopy. Chitosan has significant peaks according to the functional groups contained in its structure shown in Table 1 and Fig. 1a, which showed a stretching vibration band in chitosan in the range of 3450–3200 cm<sup>-1</sup>

| Sample code      | Chitosan solution |              | Agar-agar solution |              | Plasticiser | LiClO <sub>4</sub> |            |
|------------------|-------------------|--------------|--------------------|--------------|-------------|--------------------|------------|
|                  | Powder (g)        | Solvent (ml) | Powder (g)         | Solvent (ml) | %           | Weight %           | Weight (g) |
| CS               | 0.90              | 100          | _                  | _            | _           | 10                 | 0.1        |
| CAP <sub>1</sub> | 0.425             | 80           | 0.425              | 50           | 5           | 10                 | 0.1        |
| CAP <sub>2</sub> | 0.4               | 75           | 0.4                | 50           | 10          | 10                 | 0.1        |
| CAP <sub>3</sub> | 0.375             | 75           | 0.375              | 50           | 15          | 10                 | 0.1        |
| $CAP_4$          | 0.35              | 75           | 0.35               | 50           | 20          | 10                 | 0.1        |

 Table 1 Composition of solid polymer blend electrolyte films

corresponding to NH (primary and secondary) and hydroxyl (OH). The NHCOin pyranose ring was observed in the range of  $2880-2960 \text{ cm}^{-1}$ . The peak at  $1024 \text{ cm}^{-1}$  showed C–O stretching of polysaccharide bond (Table 2).

The ATR–FTIR studies were conducted on the blend solid polymer electrolytes film samples. The spectral details suggested that conjugated peptide bond formed by amide NH and CO groups shown in all figures, 1639, 1583, 1552, 1632, 1546, 1633, 1546, 1630, 1548 cm<sup>-1</sup>, and also obtained that the peaks at 1631, 1632, 1633, 1630 are attributed to perchlorate salt [20]. The absorption band at about 3400 cm<sup>-1</sup> is associated with O–H stretching [21].

The characteristic peak of prepared chitosan observed at 3295 cm<sup>-1</sup> is due to O–H group stretching. When there is addition of LiClO<sub>4</sub>, PEG and AA in chitosan the O–H peak has been shifted to a lower-frequency respective. This shows the formation of hydrogen bond in the blend polymer. The absorption peak at 2871, 2884, 2886, 2914, 2928 cm<sup>-1</sup> resembles CH<sub>2</sub> stretching of chitosan with blend polymer electrolytes. The peak at 1410, 1408, 1408, 1407 cm<sup>-1</sup> assigned to CH<sub>2</sub> bending of both samples [22]. A sharp strong peak due to C–O–C asymmetric stretching vibrations of an ester group of pure CS is observed at 1020 cm<sup>-1</sup>. This frequency is shifted to 1056, 1057, 1053, 1024 cm<sup>-1</sup> in the LiClO<sub>4</sub>-blended polymer electrolytes complex [23]. From these ATR–FTIR results, it can be concluded that complexation has taken place between LiClO<sub>4</sub> salt and the polymer blend.

| Absorption frequency (cm <sup>-1</sup> ) | Assignment                                       | References |
|--|--|------------|
| 3295                                     | O–H overlapped on N–H                            |            |
| 2871                                     | -CO stretching of the amide group                |            |
| 1639, 1583                               | -CO stretching of the proton amide group         |            |
| 1418                                     | O-H stretching of the CH <sub>2</sub> OH group   | [17–19]    |
| 1372                                     | -CH stretching of the CH <sub>3</sub> CONH group |            |
| 1148                                     | -C-O-C stretching of the glycosidic linkage      |            |
| 1020                                     | -C-O vibration of the polysaccharide bond        |            |

 Table 2
 FTIR spectral data of prepared chitosan

#### **HR-SEM study**

The observed structural and morphology of prepared chitosan and chitosan-based blend solid polymer electrolytes have been investigated using a high-resolution scanning electron microscopy (HRSEM). The surface morphology of the chitosan can be noted in Fig. 2 CS; it was taken with different magnifications, and different areas can exhibit almost smooth surface and layers of flakes [24–26]. Comparison of the surface morphology of solid polymer electrolytes CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub>, CAP<sub>4</sub> is shown in Fig. 2, and its composition is shown in Table 1. CAP<sub>1</sub> and CAP<sub>2</sub> reveal the perspective of some structures that have suspended out of the film surface, and the presence of uneven spherical-like structure may be due to the presence of plasticiser in the concentration of 5% and 10%, respectively, as shown in Fig. 2 [27]. Increasing the concentration of plasticiser CAP<sub>3</sub> 15% and CAP<sub>4</sub> 20% blend solid polymer electrolyte film exhibited almost homogeneous and smooth structural surface that pronounced that the salt and polymer blend is miscible with each other to show a



**Fig.2** Surface morphology characterisation of prepared chitosan and polymer electrolyte. Top view HRSEM image of the CS, CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub>, CAP<sub>4</sub> polymer blended electrolytes

uniform distribution of Li ions without any aggregation of  $LiClO_4$  particles can be observed in Fig. 2 [28, 29].

#### Energy-dispersive X-ray spectroscopy

The EDS spectrum scrutinised the composition of prepared chitosan and chitosanbased blend solid polymer electrolyte, and the result is represented in Fig. 3, and the percentage composition is tabulated in Tables 3, 4).

Figure 3 shows energy-dispersive X-ray spectra (EDS) of extracted chitosan and polymer electrolyte for CS and CAP<sub>3</sub>, which confirm the elemental composition. The EDS analysis confirms the presence of C, N, O for chitosan and C, N, O, Cl in the solid polymer electrolyte sample with no other impurity element.

#### X-ray diffraction analysis

This technique has investigated the crystalline or amorphous nature of the prepared materials. The X-ray diffraction measurements obtained for the prepared chitosan and chitosan-based blended polymer electrolyte studied in the  $2\theta$  ranging from  $10^{\circ}$  to  $80^{\circ}$  are shown in Fig. 4. It clearly says information about the nature of chitosan and intercalation of polymer salt complex with plasticiser. The diffraction pattern of extracted chitosan has 2 crystalline major peaks of strong reflections at  $2\theta=10.01^{\circ}$  and  $20.03^{\circ}$  [30] and confirms that the crystallinity of prepared chitosan is shown in Fig. 4 CS. On the addition of agar–agar in the chitosan matrix plasticised with polyethylene glycol (PEG) reduces the crystallinity of the chitosan. The interaction of hydrogen bond between chitosan, agar–agar and plasticiser with salt which partially destroying the original crystal structure of chitosan is suggested. No crystalline peaks in the blend polymer electrolytes are suggested [31] (Fig. 5).

Figure 4 CAP1, CAP<sub>2</sub>, CAP<sub>3</sub> and CAP<sub>4</sub> show the respective XRD diffractograms of blended solid polymer electrolyte systems which reveals that the effect of increasing plasticiser concentration brings a significant change in SPEs films. By the addition of PEG in the blend polymer, the XRD peak shifted at a higher angle (CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub>) up to 15% plasticiser concentration and above 15% the XRD peak shifts at a less high angle (CAP<sub>4</sub>) compared to CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub> [27]. The XRD patterns value is of CAP<sub>1</sub> (11.06, 21.05), CAP<sub>2</sub> (11.29, 21.67,



Fig. 3 EDS spectrum of CS and CAP<sub>3</sub>

| Ande VITT I CAMPI            |                  |                  |            |   |            |
|------------------------------|------------------|------------------|------------|---|------------|
| Wave number (cm <sup>-</sup> | (1-              |                  |            | Assignment  | References |
| CAP                          | CAP <sub>2</sub> | CAP <sub>3</sub> | $CAP_4$    |   |            |
| 3247                         | 3371             | 3243             | 3265       | O-H overlapped on N-H   |            |
| 2884                         | 2886             | 2914             | 2928       | -CH <sub>2</sub> stretching                                   |            |
| 1631, 1552                   | 1632, 1546       | 1633, 1546       | 1630, 1548 | -CO vibration of the amide(I,II)                              |            |
| 1410                         | 1408             | 1408             | 1407       | -CH <sub>2</sub> bending                                      |            |
| 1253                         | 1256             | 1257             | 1250       | NHCO vibrations of the amide(II)                              |            |
| 1056                         | 1057             | 1053             | 1024       | -CO vibration of the bindings C-OH, C-O-C, CH <sub>2</sub> CO | [5, 13–16] |
| 940                          | 939              | 936              | I          | Vibration of 3,6-anhydro-galactose bridge                     |            |
| 892                          | 891              | 890              | 887        | Vibration of the pyranose ring                                |            |
| 847,740                      | 775,655          | 776,654          | I          | Vibration of NH, NH <sub>2</sub>                              |            |
| 614                          | 616              | 615              | 620        | Frequency of $\delta$ (OH) out of plane                       |            |
|                              |                  |                  |            |   |            |

| Table 4Percentage compositionof CS and CAP3 | Sample           | Element | Weight % | Atomic % |
|---|------------------|---------|----------|----------|
|   | CS               | С       | 35.88    | 42.54    |
|   |                  | Ν       | 3.13     | 3.19     |
|   |                  | 0       | 60.93    | 54.28    |
|   | CAP <sub>3</sub> | С       | 32.59    | 38.88    |
|   |                  | Ν       | 5.93     | 6.06     |
|   |                  | 0       | 61.48    | 55.06    |
|   |                  | Cl      | 7.82     | 2.81     |

**Fig. 4** XRD patterns of polymer and polymer blend electrolyte CS, CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub>, CAP<sub>4</sub>



36.04), CAP<sub>3</sub> (11.53, 21.86, 36.13), CAP<sub>4</sub> (10.56, 20.01, 35.45). This may be due to the formation of intermolecular hydrogen bonding interaction between the blended polymers with the LiClO4 [32], blend chains through ion polymer interactions with lithium cations and functional groups in blend polymers, as lithium salt exhibits a cryptic nature, but CAP<sub>4</sub> has some sharp peaks that have arrived. It can be concluded that there is a some crystalline phase formed.





### Universal testing machine analysis

The mechanical properties of chitosan and blend polymer electrolytes, including tensile strength (TS), elongation (%E) and toughness, are described in using a Hounsfield H50KS, QMAT software testing machine. Specimens had a width of 25 and ~0.2000 mm thickness. The gauge length is 70 mm. The effect of plasticiser concentration changes in mechanical properties for prepared samples using solution casting method.

In this work we concluded 2 things: first we measured plasticiser-free prepared chitosan, its elongation and tensile strength, and toughness shown in Table 5. Second the amount of polyethylene glycol added in blend polymer showed a

| Sample code      | Polymer ratio  | Plasticiser<br>(PEG) (%) | Electrolyte<br>(%) | Tensile<br>stress<br>(MPa) | Elongation % | Toughness (J m <sup>-3</sup> ) |
|------------------|----------------|--------------------------|--------------------|----------------------------|--------------|--------------------------------|
| CS               | 90 wt%(CS)     | _                        | 10                 | 14.00                      | 35           | 674.75                         |
| CAP <sub>1</sub> | 85 wt%(CS+AA)  | 5                        | 10                 | 19.00                      | 6.16         | 204.69                         |
| $CAP_2$          | 80 wt%(CS+AA)  | 10                       | 10                 | 13.30                      | 7.58         | 146.99                         |
| CAP <sub>3</sub> | 75 wt%(CS+AA)  | 15                       | 10                 | 8.80                       | 9.90         | 295.54                         |
| $CAP_4$          | 70  wt%(CS+AA) | 20                       | 10                 | 7.0                        | 8.98         | 62.90                          |

 Table 5
 Tensile stress and elongation at break of chitosan and blended polymer electrolyte

conventional action of plasticisers, increasing elongation break and decreasing the tensile stress, due to a decrease in intermolecular attraction, increasing polymer mobility and reducing the intermolecular Vander Waals force of the blend polymers [33–35]. However, CAP<sub>3</sub> (15% of PEG and 75% blend polymer 10% salts) has a significant value of elongation, tensile strength and toughness than CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>4</sub>. This may be due to the stronger interaction between polyethylene glycol and blended polymer electrolytes (Fig. 6).

#### Transport number measurement by Wagner's polarisation method

In order to support the ionic conductivity data, the transference number measurements have been taken as a complimentary test for all blend polymer electrolyte samples. Transference number is one of the fundamental methods for ionic and electronic contributions of prepared polymer electrolyte system. The transference number is calculated by using the equation.

$$T_{\rm ions} = \frac{\left(I_{\rm f} - I_{\rm i}\right)}{I_{\rm i}} \tag{1}$$

$$t_{\rm c} = \frac{I_{\rm f}}{I_{\rm i}} \tag{2}$$

where  $I_i$  Initial is the total current of the ions and electron,  $I_f$  Finial residual of the electron [36] and electrons ( $t_e$ ) is calculated using Eq. 2 [37]. In the sample, a DC potential of 5 V at ambient temperature was used, containing the cell of polymer



Fig. 6 UTM studies for prepared chitosan CS, CAP<sub>1</sub>, CAP<sub>2</sub>, CAP<sub>3</sub> and CAP<sub>4</sub> polymer blended electrolyte

electrolyte membrane sandwiched between 2 blocks of stainless steel as electrodes are used in the measurement at electrochemical impedance spectroscopy (EIS) at room temperature. As well as DC voltage is passed through the sample, it is observed that the initial current rapidly falls with time due to migration of ions [38]. The polarisation method has been carried out by high ionic conductivity of blend polymer electrolyte system (CAP<sub>3</sub>). Transference number of the polymer electrolyte value measured is 0.94 (Fig. 7).

#### **Electrochemical analysis**

The electrochemical stability of the highest conductivity  $CAP_3$  blend solid polymer electrolyte was analysed using the linear sweep voltammetry with two blocking electrolyte system and a potential range of 5 V at a scanning rate of 1 mV/s. The curvature of the plot is in response to the current vs voltage [39]. Electrochemical stability of the polymer electrolyte membrane is stable up to 3.1 V in the literature review based on iota-carrageenan [38] in our work; CAP<sub>3</sub>solid polymer electrolyte film stable up to 3.3 V is observed and beyond that electrolyte was decomposed. Figure 6 shows the linear sweep voltammogram curve of the CAP<sub>3</sub> system (Fig. 8).

#### AC impedance analysis

The electrochemical impedance spectroscopy (ESI) analysis is the most powerful technique for characterising the electrical properties of the prepared CS and blend solid polymer electrolyte samples. In polymer electrolyte system, impedance spectra have been obtained at room temperature. Nyquist plot for CS,  $CAP_{1}$ ,  $CAP_{2}$ ,  $CAP_{3}$ , and  $CAP_{4}$  was fitted with an equivalent circuit (line) to estimate the bulk resistance



Fig. 7 Wagner's method polarising current for polymer electrolyte CAP<sub>3</sub>



Fig. 8 Linear sweep voltammogram of the highest conducting salted and plasticised membrane

of the polymer electrolyte. The ionic conductivity of the blend polymer electrolyte films was calculated using the formula given below

 $\sigma = L/RbA$ 

where  $\sigma$  ionic conductivity, L = thickness, A = contact area, Rb = bulk resistance. The decrease of  $R_b$  value leads to the enhanced ionic conductivity after the introduction of plasticiser in blend polymer electrolyte because of the reduction of crystalline nature of chitosan matrix, as shown in the XRD studies [40]. Ionic conductivity plays one of the significant roles for the availability of the mobility of lithium ions in the polymer blend matrix during the electrochemical device.

Table 6 shows that the ionic conductivity of the CS and blend solid polymer electrolyte, CAP<sub>3</sub> has maximum ionic conductivity value than the CS, CAP<sub>1</sub>, CAP<sub>2</sub>, and CAP<sub>4</sub>. The ionic conductivity of CAP<sub>3</sub> is influenced by plasticising of CS and AA blend polymer using PEG. The ionic conductivity increases with increases in plasticiser composition of blended solid polymer electrolytes due to reduced crystallinity of Chitosan (Fig. 9).

| Sample code      | Polymer with perchlorate ratio     | Plasticiser (%) | Ionic<br>conductivity<br>Scm <sup>-1</sup> |
|------------------|------------------------------------|-----------------|--|
| CS               | CS 90% + 10%LiClO <sub>4</sub>     | _               | $5.91 \times 10^{-5}$                      |
| CAP <sub>1</sub> | CS-AA 85% + 10%LiClO <sub>4</sub>  | PEG-5           | $1.8 \times 10^{-4}$                       |
| CAP <sub>2</sub> | CS-AA 80% + 10%LiClO <sub>4</sub>  | PEG-10          | $2.8 \times 10^{-4}$                       |
| CAP <sub>3</sub> | CS-AA 75% + 10%LiClO <sub>4</sub>  | PEG-15          | $4.56 \times 10^{-4}$                      |
| CAP <sub>4</sub> | CS-AA 70% + 10% LiClO <sub>4</sub> | PEG-20          | $2.01 \times 10^{-4}$                      |

 Table 6
 Ionic conductivity of blend polymer electrolytes at room temperature



Fig. 9 Ionic conductivity of blend solid polymer electrolytes

### Conclusions

In this investigation, bioactive polymer chitosan was prepared from shrimp shells which is fairly soluble in acetic acid with adequate physical–chemical properties. Chitosan-based blend solid polymer electrolyte plasticised with various weight percentages of polyethylene glycol (PEG) and the LiClO<sub>4</sub> was successfully prepared by a solution casting method. FTIR studies revealed the complexation between polymer blend and lithium salt. X-ray diffraction results showed that the prepared composite having composition CAP<sub>3</sub> was highly amorphous in nature. The surface morphology of the prepared chitosan and chitosan-based blend solid polymer electrolyte was studied using high-resolution scanning electron microscopy. Further, mechanical studies showed that the prepared blend polymer electrolyte, CAP<sub>3</sub>, has comparatively high elongation behaviour.

The ionic conductivity results revealed that the addition of plasticiser composition plays vital role in conductivity values. The enhancement in ionic conductivity value can be attributed to the increase in chain flexibility in CS–AA–LiClO4 electrolyte with the presence of polyethylene glycol. The maximum ionic conductivity of CAP<sub>3</sub> ( $4.6 \times 10^{-4}$  Scm<sup>-1</sup>) is measured for the blend polymer electrolyte with composition of 75% (CS, AA), 15% PEG, 10% LiClO<sub>4</sub> at room temperature. Also, the transference number of ions for the polymer electrolyte measured using Wagner's polarisation method showed that the CAP<sub>3</sub> polymer electrolyte exhibits the highest conducting sample measured by linear sweep voltammetry and film was stable up to 3.3 V, and then, the electrolyte was decomposed on further applying voltage. All these results implied that the prepared solid polymer electrolyte can be effectively used as a promising material for the fabrication of solid-state lithium-ion batteries.

**Acknowledgements** We are acknowledging Dr. Amirthavalli Raghupathy Memorial Fund for providing support (Muffle Furnace Instrument) for our research laboratory. Also, authors would like to acknowledge Department of chemical engineering, IIT Madras, for providing characterisation facility using HR-SEM.

#### Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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