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Evaluation of Conducting Properties of Biopolymer Electrolyte K-Carrageenan with The Effect of Three Different Ammonium Salts

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ABSTRACT. In the present work kappa-carrageenan (KC) with different ammonium salts NH_4Cl, NH_4Br, and NH_4I membrane were successfully synthesized by the solution casting technique. The prepared eco-friendly membrane is subjected to ionic conductivity study, XRD study, transference number studies, and then it's compared. The ionic conductivity value for KC with 200 mg NH_4Cl is 1.81×10^{-4} S/cm, KC with 300 mg NH_4Br is 2.80×10^{-3} S/cm, KC with 400 mg NH_4I is 5.88×10^{-5} S/cm. Among all the three, combinations the KC with 300 mg NH_4Br gives high ionic conductivity. From the X-Ray Diffraction pattern, KC-NH_4Cl incorporation greatly enriched the amorphous region. All the three membranes transference numbers are very close to unity. Among all the three combinations, KC with 300 mg NH_4Br is the best combination for the application of fuel cell battery.

Keywords: kappa-carrageenan, Ammonium salts, Electrolytic conductivity, Ionic Transport.

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1. INTRODUCTION

The conductivity of a material is the major property of electrical appliances. The conductivity of the material is different for different materials. Production of electricity in the material depends on the dissolved impurities in the material. Depending upon the suspended ions the electrical charge is transferred in the material. Based on conductivity and resistivity, the conducting material is segregated into two main categories. The first one is the highest conductivity or lowest resistivity materials and the second one is the lowest conductivity or highest conductivity materials. In the field of electrical engineering applications, both the highest conducting materials and the lowest conducting materials play a vital role. The low conducting materials like carbon, tungsten are useful to fabricate the heating elements. The material of low resistivity and high conductivity is useful for an electrical machine, transmission, and distribution of electrical energy. Here our aim is to find the highest conducting material for energy-saving devices. The Highest conducting materials have the properties of the lowest possible resistance, the highest possible conductivity, good mechanical strength, stability, corrosion-free, low cost, long life, and a high elasticity [1, 2, 3]. The belongings of conducting material are varying for various purposes. The present work is to find a flexible, high conducting solid biopolymer. Because of the applications of the bio-polymer membranes in the fields of electronics, fuel cells, solar cells, batteries are increasing day by day. Compared to metal like silver, gold, and aluminum conductivity, polymers have low electrical conductivity reported by the researches in 1970 [4]. Nowadays the conductivity of polymer is increased the best selection of polymers and added impurities [5, 6, 7]. Kappa carrageenan solid polymer electrolytes [SPE] have a great attention in many electrolyte applications due to several good advantageous properties like ease of fabrication, flexibility in nature, cost effectiveness, good mechanical stability, and safety in use. To reduce environmental pollution, bio-based polymers are developed as electrolytes. It is one of the primary resources for recycling energy [8]. From the literature survey, we found a conductivity value for pure Kappa carrageenan of 6.76×10^{-6} S/cm at room temperature [1]. The selection of dopant is another goal to reach the highest conducting flexible biopolymer. We have selected a proton-conducting ammonium salts to achieve the highest conducting electrolyte. As we expected, prepared biopolymer conductivity increased [9].

In this present work, we have synthesized the biopolymer membrane by the choice of kappa carrageenan with different kinds of ammonium salts (NH_4Cl, NH_4Br, and NH_4I) [5].

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2. MATERIALS AND METHODS

2.1. Chemicals

Chemicals selected for this work are the biopolymer kappa-carrageenan (KC) [6] and NH_4Cl, NH_4Br, and NH_4I, which were purchased from TCI Chemicals, Coimbatore, Tamil Nadu.

2.2. Biopolymer Electrolyte Preparation

Biopolymer electrolytes were prepared by the solution casting method. The solution is prepared by using water as a solvent. First, prepare a fixed amount (1 g) of kappa carrageenan solution and different concentrations (200 mg, 300 mg, 400 mg) of ammonium salt (NH_4Cl, NH_4Br, NH_4I) solutions. Now mix 1 gm KC with 200 mg solutions and allow them to stir continuously without forming any bubbles. Similarly prepare the solutions for different concentrations. The solutions were prepared at room temperature. Then the solutions are transferred into petri dishes, which are then kept inside the oven to maintain the temperature range of 45°C. After all this processing, transparent and flexible biopolymer membranes were obtained.

2.3. XRD

The materials phase transformation from crystal to polymer is studied by PANalytical X' pert Pro powder X'celerator Diffractometer instrument. The membranes were measured in the range of 10 to 80 degrees in 2θ.

2.4. Electrolytic conductivity:

The electrolytic conductivity of three different ammonium salts in kappa-carrageenan was analyzed by the formula of

$$\sigma = t/AR_b \text{ (S/cm)}$$

Where't' and 'A' are the thickness and area of the polymer electrolyte film respectively. R_b is the bulk resistance of the polymer membrane [10].

2.5. Ionic Transport Analysis

Ionic transference numbers are calculated by the below-mentioned equation, and it is determined by the Wagner procedure [11].

$$T_{ion} = (I_{initial} - I_{final})/ I_{initial}$$

In this procedure fixed DC voltage of 1.8 V is applied across the cell.

3. STUDIES AND ANALYSIS

3.1. XRD Discussion

The intensity of the peaks in pure Kappa carrageenan decreases when we add 200mg NH_4Cl. And the beaks are shifted to wide-angle value [7] by the addition of 300mg NH_4Br and 400mg NH_4I salts. Figure 1 shows the amorphous range of prepared biopolymers. The interaction between used salts and biopolymers results in a merely increased amorphous nature from pure to doped electrolyte. The maximum amorphous nature is observed in 1 g of KC and 200 mg of NH_4Cl-doped electrolyte. The broadening of the spectrum at 300mg NH_4Br and 400mg NH_4I salts. This is because the biopolymer was unable to accommodate the used salt, which leads to the recombination of the ions [9].

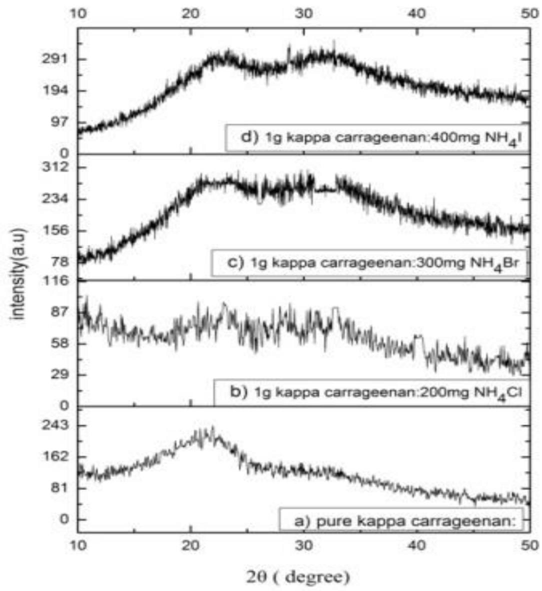

Fig.1. Amorphous nature of Pure and ammonium salts doped membrane

Compared to pure KC, 200 mg NH_4Cl, 300 mg NH_4Br, 400 mg NH_4I added electrolytes are having a more amorphous phase which may enhance the ionic conductivity of the biopolymer electrolyte [7]. From the XRD analysis, we find the selected highest conducting biopolymer electrolytes are having a polymer nature, and it has better ionic conductivity.

3.2. Electrolytic conductivity

The Cole-Cole plots of the pure kappa-carrageenan and ammonium salts doped kappa-carrageenan biopolymer electrolytes are shown in figure 2.

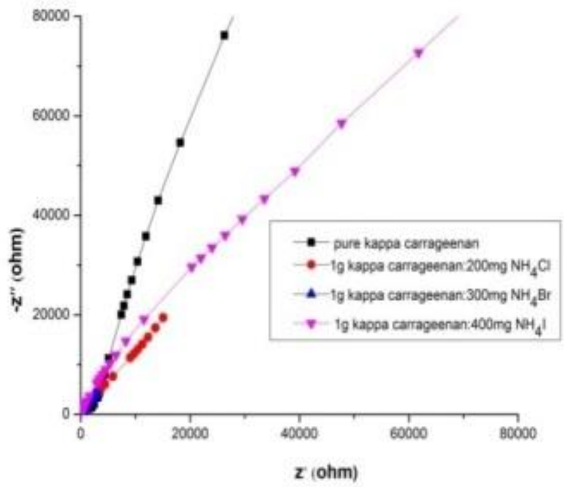

Fig.2. Cole-Cole plots of the pure kappa-carrageenan and ammonium salts doped membrane.

The ionic conductivity value for 1gm kappa with 200 mg NH_4Cl is 1.81× 10^{-4} S/cm,1gm kappa with 300 mg NH_4Br is 2.80× 10^{-3}S/cm, 1gm kappa with 400 mg NH_4I is 5.88× 10^{-5} S/cm. 200 mg of NH_4Cl, 300mg of NH_4Br, and 400mg of NH_4I salt concentrations are well incorporate with the 1 g of KC. Beyond the addition of 200 mg of NH_4Cl, 300mg of NH_4Br, and 400mg of NH_4I salt concentrations, the Cole–Cole plot indicates the resistive component exits in the polymer electrolyte and is corresponding to the mobile ion being less in the polymer [12]. Among all the three, combinations the 1gm K-carrageenan with 300 mg NH_4Br gives the high ionic conductivity in the order of 2.80× 10^{-3} S/cm. Figure 3 drawn for the conductivity of prepared biopolymer membranes with different concentrations of ammonium salts. Calculated ionic conductivity as a function of ammonium salts.

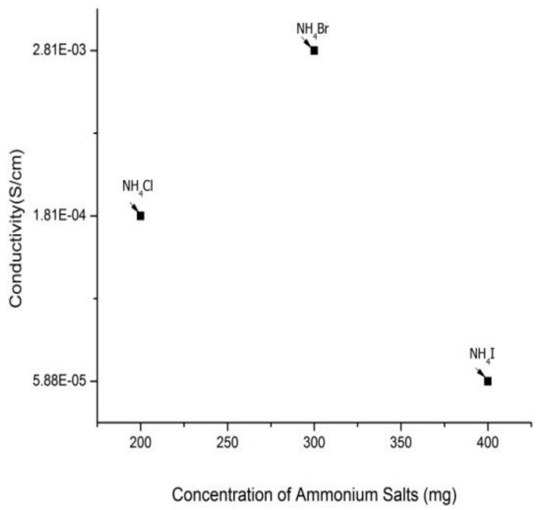

Fig.3. Variation of conductivity as a function of ammonium salts.

3.3. Ionic Transport Analysis

The initial polarization currents of all three membranes are decreases with time due to the depletion of the ionic species in the electrolyte and finally, it is constant in the fully depleted situation. This is because the ionic current through an ion-blocking electrode falls rapidly with time. The initial current for the present study of 1gm K-carrageenan with 200 mg NH_4Cl, 300 mg NH_4Br, and 400 mg NH_4I are 110 µA, 230 µA, and 170µA respectively. Calculated transference numbers are very close to unity. The Polarization verses time graph is shown in figure 4.

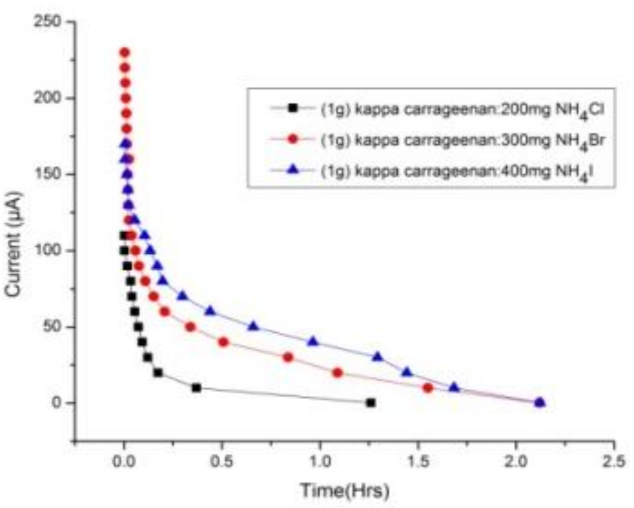

Fig. 4. Polarization current verses time for prepared bio polymer Membrane.

4. CONCLUSION

Kappa-carrageenan (KC) with different ammonium salts NH_4Cl, NH_4Br, and NH_4I membrane were successfully synthesized by the solution casting technique.

From the conductivity studies, the maximum ionic conductivity of prepared biopolymer film was 2.80× 10^{-3} S/cm, it is achieved for the membrane doped with 300 mg NH_4Br salt concentration. Due to the better conductivity and mobility, this biodegradable kappa carrageenan based flexible solid electrolytes in association with conducting salts were used in different bio polymer battery [13] assemblies.

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