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Development of Red Seaweed extracted film for energy saving Batteries

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ABSTRACT

Red seaweed extract, kappa-carrageenan (KC) is used to fabricate a flexible battery with an ammonium salt. A combination of the film was successfully synthesized by the Solution Casting technique. The prepared eco-friendly film is subjected to ionic conductivity study, transference number studies, and then the high response film is used to fabricate battery. The highest ionic conductivity value for 1gm kappa-carrageenan with 200 mg NH_4Cl is 2.99 × 10^{-4}S/cm. The highest conducting seaweed extract film transference numbers are very close to unity. By using this biopolymer film, the fabricated biopolymer battery generates the maximum of open-circuit voltage is 1.74V. By using this proton ion battery we can replace liquid ion battery and solid ion battery. Also, the films are easily biodegradable and not at all generate e-waste.

Keywords: Red seaweeds extract, Kappa-carrageenan, Flexible film, Conductivity, Battery fabrication

INTRODUCTION

In a green economy, the demands for biopower enhance the technological interest in the field of solid biopolymer electrolyte (BPE). In recent years, this highly specialized field encompasses to play a vital role in designing energy-based devices, replacing liquid electrolyte in fuel cells, electrochemical sensors, batteries, and electrochromic devices[1-8]. The Solid BPE provides good contact surface with electrodes, good shelf life, less problem with leakage or pressure distortion and also the BPE is easy to prepare and very affordable[9,10,11]. However, the synthetic polymer faces disadvantage and not being environmentally green. Hence, it is imperative to develop the biopolymer electrolytes by using natural polymer, which has gained more and more attention, owing to their abundant in nature, low cost, friendliness to the environment and potential as a substitute for some petrochemicals[12]. In this way, an ideal solid BPE in the polymer electrolyte system contributes to free pollution and it has directly brought forward green nation, which fosters the interest in research to address the environmental crises. Several researchers are doing their research in the field of biopolymer using starch[13-14], cellulose, chitosan, pectin, agar, and Kappa-carrageenan.

Kappa-carrageenan extracted from red seaweed alga to form complex arrangements. The use of this to form thin flexible film and is used to fabricate battery devices. Fabrication of thin-film battery is an emergent field in the year 2019 to 2029.[15]

Biopolymer films are mechanically behaving like a solid but the conductivity behavior is like a liquid state.[16] 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

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or lowest resistivity materials and the second one are 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 battery fabrication. 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[17-19]. Conducting materials are varying for various purposes. The present work is to find a flexible, high conducting solid biopolymer electrolyte. Because of the applications (electronics, fuel cells, solar cells, and batteries) of bio-polymer membranes, researches are increasing day by day. From my literature, there is less usage of red seaweed kappa-carrageenan in the field of battery fabrication. But the property of kappa carrageen is suitable for the current scenario. Because KC is a biopolymer and it is biodegradable, eco-friendly and available. And also, KC has good electrical and mechanical property. The conductivity of pure kappa-carrageenan is increased by the best selection of added impurities. The selection of impurity is another target to achieve the highest conducting flexible biopolymer. Proton conductors are difficult to achieve because of its transport property discovered in 1990s[20] even though, we have selected a proton-conducting NH_4Cl to achieve the highest conducting electrolyte. As we expected, prepared biopolymer conductivity increased two order magnitudes by adding NH_4Cl to kappa carrageenan.

In this present work, we have synthesized the biopolymer film by the new choice of red seaweed extracted biopolymer kappa carrageenan with different concentration of ammonium NH_4Cl[21]. Then the highest conducting electrolyte is used to fabricate the proton-conducting battery.

Experimental

Chemicals:

Chemicals selected for this work is red seaweed extracted kappa-carrageenan (KC)[22] and NH_4Cl were purchased from TCI chemicals.

Biopolymer Film Electrolyte Preparation

For Kappa Carrageenan+Ammonium Chloride (KC+NH_4Cl) biopolymer electrolyte film preparation, Kappa Carrageenan ($C_{24}H_{36}O_{25}S_2^{-2}$) (M.W = 788.7 g/mol), salt ammonium chloride (NH_4Cl) (M.W = 53.491 g/mol) purchased from TCI chemicals private Ltd., Tamilnadu, India. And the solvent distilled water (H_2O) (M.W = 18.015 g/mol) has been Used for this electrolyte preparation. The biopolymer electrolyte has been prepared by dissolving KC and NH_4Cl in distill water and mixtures are thoroughly stirred to obtain a homogenous mixture. The mixture is then poured on a polypropylene dish and dried in the oven at 40 °C for 1 day to ensure the removal of solvent traces. After drying the films have been peeled from Petri dishes. The film thickness of the KC: NH_4Cl biopolymer electrolyte is in the range of 0.01265-0.01275 cm. These biopolymer electrolytes have been characterized by different experimental techniques. The different biopolymer electrolyte systems prepared are:

1gm KC
1gm KC:100mg NH_4Cl
1gm KC:200mg NH_4Cl
1gm KC:300mg NH_4Cl

Characterization Techniques

X-ray diffraction (XRD) analysis

The amorphous nature of biopolymer electrolytes has been investigated using XRD. The XRD patterns of the films were recorded at room temperature by X' pert pro diffractometer system using the Cu-kα radiation in the range of 2θ= 10° to 50°.

Differential scanning calorimetry (DSC)

The thermal stability of the BPE's has been studied using DSC Q20 V4.10 build 122 with a resolution of 0.01 mg. The films were taken in an aluminum pan and heated upto 500 °C with the heating rate of 5 °C per minute under controlled air atmosphere and the films were purged using a nitrogen atmosphere during the measurements. Dry nitrogen gas at the rate of 50 ml/min has been purged through the cell during the thermal treatment.

Impedance spectroscopy

Impedance analysis has been performed using impedance spectrometer, which is a powerful method for characterizing the ionic conductivity of freshly casted samples. Prior testing, the thickness of the films was measured by using a digital screw gauge. Then, films with well known thickness (0.01265-0.01275 cm) have been sandwiched between two stainless steel blocking electrodes and tested using HIOKI 3532 in the range of 42 Hz-1 MHz with various temperatures from 303 k to 343 k.

Fabrication of proton battery

Using the highest conducting BPE 1gm KC: 200mg NH_4Cl a proton battery have been constructed and their results are discussed.

Results and Discussion

X-ray diffraction (XRD) analysis

Figure 1 shows the XRD patterns of pure KC and KC with different concentrations of NH_4Cl. The XRD patterns indicate that the solid polymeric films were contain amorphous phases, which make the polymeric films to be in flexible in nature.

The figure 1 indicates that the amorphous nature of doped polymer KC increases, when the NH_4Cl salt is incorporated into the KC matrix. The XRD patterns also indicates that the broadness of peak increases and its relative intensity decreases with increase of NH_4Cl concentration, which reveals that as ion concentration in the electrolyte increases, both the fraction of amorphous phase and charge carriers increases simultaneously[23]. From the XRD graph it has been noted that 1gmKC:200mg NH_4Cl has maximum amorphous nature. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the

polymer electrolyte resulting in high ionic conductivity[24]. On further addition of NH_4Cl concentration, the intensity of peaks increases for 1gm KC: 300mg NH_4Cl, which indicates the increase in crystallinity. This is because the polymer host was unable to accommodate the salt, which leads to the recombination of the ions.[25]

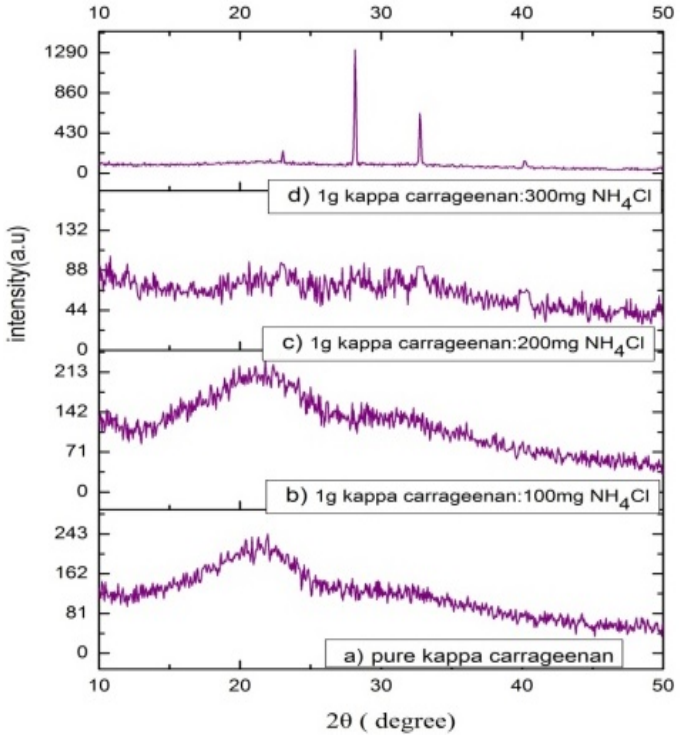

Figure 1. XRD pattern for (a) pure KC, (b) 1gm KC: 100mg NH_4Cl, (c) 1gm KC: 200mg NH_4Cl, (d) 1gm KC: 300mg NH_4Cl.

Differential scanning calorimetry (DSC)

DSC analysis was carried out to measure the glass transition temperature (T_g) of polymer electrolytes. The change in T_g of KC due to the addition of salt (NH_4Cl) as shown in Figure 2**.** The T_g of pure KC was obtained at 41.59 °C. The T_g value was obtained as 36.95°C, 29.16°C and 38.40°C for the membrane 1gmKC: 100mgNH_4Cl, 1gmKC:200mgNH_4Cl and 1gmKC:300mgNH_4Cl respectively. The T_g values of prepared polymer electrolytes are tabulated in Table 1.

Table 1 Glass Transition Temperature of prepared polymer electrolytes

Polymer composition	T_g (°C)
1gm Pure KC	41.59
1gm KC:100mg NH_4Cl	36.95
1gm KC:200mg NH_4Cl	29.16
1gm KC:300mg NH_4Cl	38.40

The DSC curve in figure 2 indicates that the T_g value of KC increases corresponding to the increase in the concentration of (100mg) NH_4Cl and decreases with the concentration of 200mg NH_4Cl. In general, the decrease in glass transition temperature increases ionic conductivity. There are two factors involved in the increase of T_g with the salt content: (1) interaction of H^+ with the polar group of the polymer increases the micro viscosity of the solid biopolymer electrolyte, and (2) the polymer chain is expanded by the introduction charges on the polymer chain because of the electrostatic repulsion. This behavior has been interpreted as a consequence of a reduction in segmental motion caused by an increase in intermolecular and intermolecular co-ordinations between H^+ cations and the oxygen atoms in the polymer chain.[26]

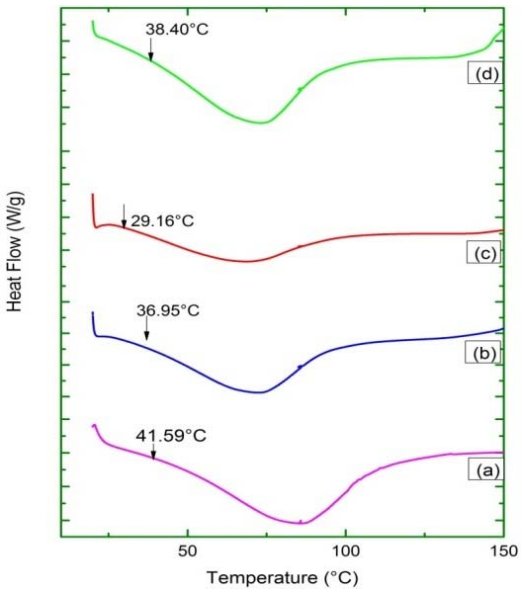

Figure 2. DSC thermo grams of (a) pure KC, (b) 1gm KC: 100mg NH_4Cl, (c) 1gm KC: 200mg NH_4Cl, (d) 1gm KC: 300mg NH_4Cl.

Impedance spectroscopy

Generally, the impedance plot consists of a distorted semicircle in the high-frequency region followed by an inclined spike in the low-frequency region. The high-frequency semicircle is due to the parallel combination of bulk resistance (due to migration of ions) and bulk capacitance (due to immobile polymer chain). The low-frequency spike represented by a constant phase element is due to the formation of double-layer capacitance at the electrode-electrolyte interface. The electrolytic conductivity of NH_4Cl 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[27]. The Cole-Cole plots of the pure kappa-carrageenan and ammonium salts doped kappa-carrageenan biopolymer electrolytes are shown in figure 3.

The bulk resistance values were obtained from Cole - Cole plot which were listed in Table 2.

In Table 2, the resistance value of pure KC was obtained as $1.75\times10^3\Omega$, whereas for 200mg of NH_4Cl doped with 1gm KC polymer electrolyte the value of resistance was decreased from $1.75\times10^3\Omega$ to 351Ω. The highest conductivity polymer electrolyte 1gm KC:200mg NH_4Cl has R_b = 351Ω.

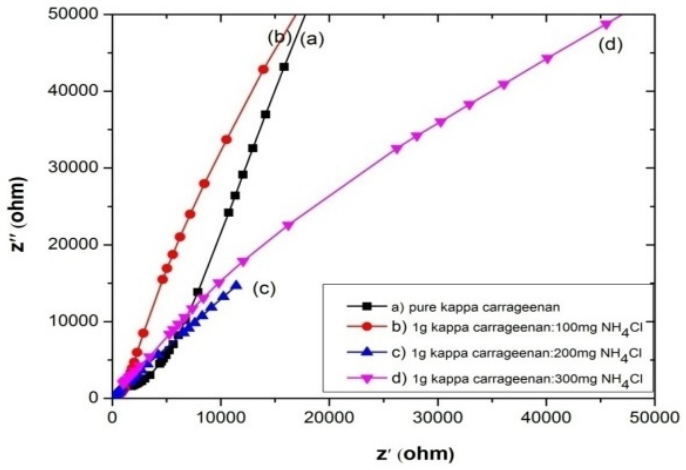

Figure 3. Cole - Cole plot of red seaweed extract kappa carrageenan with NH_4Cl

Table 2 Resistance value for all polymer electrolytes

Polymer composition	R, (Ω)
1gm Pure KC	1.75×10^{3}
1gm KC:100mg NH_4Cl	6.81×10^{2}
1gm KC:200mg NH_4Cl	3.51×10^{1}
1gm KC:300mg NH_4Cl	9.89×10^{2}

The calculated ionic conductivity for different concentrations of KC:NH_4Cl polymer electrolytes were listed in Table 3 for various temperatures.

Table 3 Ionic conductivity data and activation energy values for KC:NH_4Cl polymer electrolyte for different temperature.

Polymer composition	$\sigma_{303\ k}$	$\sigma_{313\ k}$	$\sigma_{323\ k}$	$\sigma_{333\ k}$	$\sigma_{343\ k}$	Activation energyEa (ev) at room temperature
Pure KC	6.03×10^{-6}	6.11×10^{-6}	7.37×10^{-6}	7.38×10^{-6}	9.78×10^{-6}	0.01273
1gm KC:100mg NH_4Cl	1.55×10^{-5}	1.59×10^{-5}	1.63×10^{-5}	1.84×10^{-5}	2.08×10^{-4}	0.06558
1gm KC:200mg NH_4Cl	2.99×10^{-4}	3.10×10^{-4}	3.18×10^{-4}	3.27×10^{-4}	3.30×10^{-4}	0.02295
1gm KC:300mg NH_4Cl	1.07×10^{-5}	1.08×10^{-5}	1.13×10^{-5}	1.16×10^{-5}	1.22×10^{-5}	0.029840

Table 3 indicates that among the various concentrations of KC:NH_4Cl polymer electrolyte the 1gm KC:200mg NH_4Cl polymer electrolyte has highest ionic conductivity (2.99×10^{-4}S cm^{-1}) at room temperature, which also has a greater conductivity than that of pure KC (6.03×10^{-6} S cm^{-1}). The higher ionic conductivity of 1gm KC:200mg NH_4Cl may be arises due to the transition from semicrystalline phase to an amorphous phase of the polymer complex and increase in charge carrier concentration.[28]

IONIC TRANSPORT ANALYSIS:

Ionic transference numbers are calculated by the below-mentioned equation, and it is determined by the Wagner procedure.[29]

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

In this procedure, A fixed DC voltage of 1.8 V is applied across the cell. The initial polarization current (110 μA) of the membrane is decreased 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. Calculated transference numbers are very close to unity. That means the prepared film for battery fabrication is highly polarized. Figure 4 shows the Polarization current versus time plot for 1gm KC:200mg NH_4Cl.

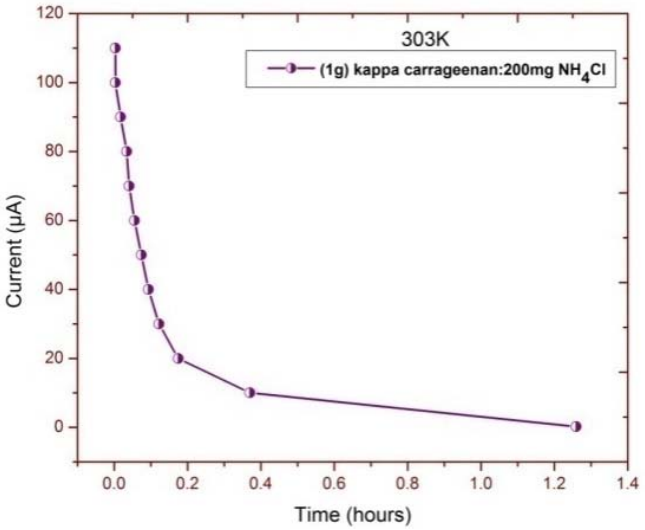

Figure 4. Polarization current vs time plot for 1gm KC:200mg NH_4Cl.

FABRICATION OF SOLID PROTON BATTERY

For a battery fabrication Anode is formed by zinc sulfate, graphite, and zinc powder. The cathode is formed by vanadium pentaoxide, graphite, lead oxide, 1gm kappa carrageenan and 200

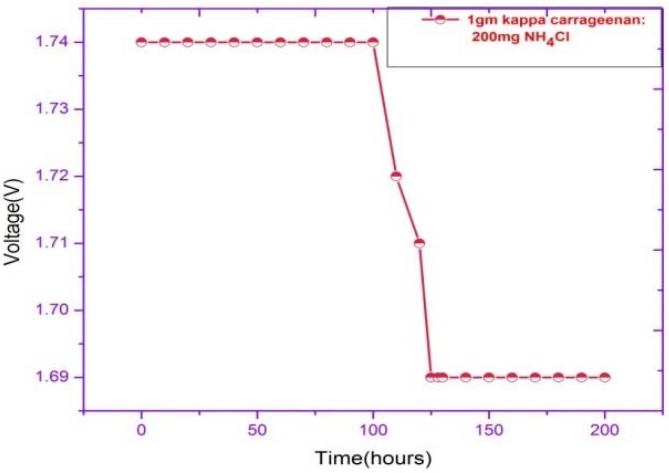

Figure 5. Open circuit voltage and discharge curve for the cell as a function of time for 1gmKC:200mgNH_4Cl polymer electrolyte.

mg NH_4Cl. Both anode and cathode compounds are pelletized to form a thin pellet. Prepared solid biopolymer electrolyte is positioned between prepared anode and cathode, and this arrangement is situated in the battery holder[30]. In this work the cell gave voltage of E = 1.74 V. The open-circuit voltage (OCV) and discharge behavior of the cell with time was shown in figure 5, which indicates that the cell potential decreases during discharge. The initial sharp decrease in voltage may be due to polarization and it remains constant of 1.69 V for a particular duration after. The region in which the voltage remains constant is called the plateau region.

CONCLUSION

Red seaweed extract Kappa Carrageenan has unique physical properties, powerful water reaction, plentiful functional groups. Worldwide use of non-toxic kappa carrageenan, research has focused to make it versatile biopolymer for blending it with other ammonium salts to explore novel applications in solid-state polymer battery[6]. Due to the better conductivity and mobility, these biodegradable kappa-carrageenan based flexible solid electrolytes in association with conducting salts were used in different biopolymer battery[11] assemblies. The highest conducting biopolymer electrolyte kappa carrageenan with NH_4Cl film is used to construct the power saving battery.

Conflict of Interest: Authors declare no conflict of interest.

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