Journal of Non-Crystalline Solids 481 (2018) 424–434

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Conductive bio-polymer electrolyte iota-carrageenan with ammonium nitrate for application in electrochemical devices

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ARTICLE INFO

Keywords:
Bio-polymer
Ammonium nitrate
XRD
FTIR
DSC
AC impedance
LSV
Proton battery
Fuel cell

ABSTRACT

Bio-polymer electrolyte iota-carrageenan (I-carrageenan) with ammonium nitrate (NH_4NO_3) has been prepared by solution-casting technique. The increase in amorphous nature of the bio-polymer electrolyte due to the addition of salt has been confirmed by X-ray diffraction analysis. From the XRD spectra, the average particle size has been calculated using the Debye–Scherrer formula and the value is 0.98 nm. The complex formation between the polymer and the salt has been confirmed by Fourier transform infra-red spectroscopy. The glass transition temperature of the bio-polymer I-carrageenan with NH_4NO_3 electrolytes has been found using differential scanning calorimetric technique. From the AC impedance spectroscopic analysis, the ionic conductivity value has been found to be 1.46×10^{-3} S/cm at ambient temperature for the composition of 1.0 g I-carrageenan: 0.4 wt% NH_4NO_3. The temperature dependent conductivity of the polymer electrolyte obeys an Arrhenius relationship. The dielectric behavior has been analyzed using dielectric permittivity (ε^*) and the relaxation frequency (τ) has been calculated from the loss tangent spectra (tan δ). The modulus spectra indicate non-Debye nature of the material. Ionic transference number has been found to be 0.95 for the polymer 1.0 g I-carrageenan: 0.4 wt% NH_4NO_3. The result reveals that the conducting species are predominantly due to ions. Electrochemical stability window of 2.46 V has been measured by using linear sweep voltammetry for the highest ionic conducting membrane. A primary proton battery has been constructed with the highest conductivity sample and open circuit voltage has been found to be 1.04 V. Fuel cell has been constructed with the highest proton conductivity polymer 1.0 g I-carrageenan: 0.4 wt% NH_4NO_3 and the open circuit voltage found to be 442 mV.

1. Introduction

Solid polymer electrolytes are generally being used in electrochemical devices due to its dimensional stability, flexibility, electrochemical stability, safety and long life span [1]. Considerable interest has been focused on the development of proton conducting polymer electrolyte for fuel cell. Normally, Nafion is used as a membrane for proton conduction [2]. Nafion is however costly, making the fuel cell fabricated from it also costly. To reduce the cost of the fuel cell, developing new and novel proton conducting membrane materials capable of conducting protons with higher ionic conductivity, better mechanical strength, lower cost, and durability is an important issue. Different polymeric electrolyte systems have been extensively studied and most of them are based on poly (ethylene oxide), poly (vinyl pyrrolidone), poly (vinyl alcohol), poly (acrylonitrile), poly (methyl methacrylate), poly (vinyl chloride), and other synthetic polymers. Recently, researchers all over the world have started focusing on proton conducting polymer electrolyte for energy storage devices. Additionally, they have started to prepare eco-friendly biodegradable bio-polymer electrolytes. The bio-polymers are the polymers derived from the naturally occurring renewable sources. These bio-polymer electrolytes are cost-effective, and eco-friendly. These advantages have made the bio-polymer electrolytes a promising substitute for synthetic polymers in fuel cells.

Among the bio-polymers, starch, cellulose, chitosan, pectin, agar-agar and carrageenan are of interest. Since they are abundant in nature, renewable, biocompatible and cost effective. Khiar and Arof [3] have reported conductivity value of $3.89 \pm 0.79 \times 10^{-5}$ S/cm for starch/chitosan NH_4NO_3 polymer electrolyte. Proton conductivity value of $9.93 \pm 1.90 \times 10^{-3}$ S/cm for plasticized chitosan with NH_4NO_3 has been reported by Ng and Mohamad [4]. Noor and Isa [5] have reported proton conductivity value of 6.48×10^{-5} S/cm for carboxymethyl cellulose (CMC) with NH_4SCN. The conductivity value of 7.71×10^{-3} S/cm for carboxymethyl cellulose with NH_4NO_3 has been

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https://doi.org/10.1016/j.jnoncrysol.2017.11.027
Received 15 September 2017; Received in revised form 28 October 2017; Accepted 15 November 2017
Available online 22 November 2017
0022-3093/

reported by Kamarudin et al. [6]. Proton conductivity value of 1.02×10^{-3} S/cm for cellulose acetate with NH_4NO_3 has been reported by Monisha et al. [7]. Selvalakshmi et al. [8] has presented proton conductivity value of 1.03×10^{-3} S/cm for agar-agar with NH4SCN. Premalatha et al. [9] have reported proton conductivity value of 2.85×10^{-4} S/cm for tamarind seed polysaccharide with NH_4SCN. Proton conductivity value of 1.09×10^{-3} S/cm for agar-agar with NH_4NO_3 for fuel cell application has been reported by Boopathi et al. [10]. The loosely bound proton of the ammonium ion is responsible for conductivity in these polymer complexes.

Carrageenan is linear polysaccharides extracted from *Chondrus crispus* seaweed, it is non-toxic and biodegradable. Carrageenan dissolves readily in hot water and forms film easily. Carrageenans are widely used in the food, pharmaceutical and cosmetic industries. There are three types of carrageenans are available depending on the number and position of the ester sulfate groups, termed iota carrageenan (i) ($C_{24}H_{34}O_{31}S_4{}^{-4}$) kappa (k) carrageenan ($C_{24}H_{36}O_{25}S_2{}^{-2}$) and lambda (λ) ($C_{12}H_{19}O_{20}S_3{}^{-3}$) carrageenan. Since carrageenan is rich with hydroxyl groups in its structures and it has oxygen atom which is important to form a coordinated bond with cations. C.A. Ng et al. [11] reported a conductivity value of 3.25×10^{-4} S/cm for a polymer electrolyte based on kappa-carrageenan and cellulose derivatives for solar cell applications. Carrageenan was reported by Liang Li and Sonia Lefnooui [12] for drug delivery applications. Jumaah et al. [13] has reported that the ionic conductivity value of 4.87×10^{-6} S/cm for iota carrageenan and 2.19×10^{-8} S/cm for carboxymethyl cellulose/I-carrageenan. N. E. A. Shuhaimi [14] reported a polymer-salt complex made from chitosan, k-carrageenan and ammonium nitrate achieved a conductivity value of 2.39×10^{-4} S/cm. A conductivity value of 1.08×10^{-3} S/cm for iota-carrageenan with NH_4Br was reported by Karthikeyan et al. [15].

In the literature, very less work has been reported using iota carrageenan with ammonium salts. The main purpose of this work is to prepare polymer membrane, I-carrageenan with different concentration of ammonium nitrate (NH_4NO_3) and its characterization with different technique such as X-ray diffraction analysis (XRD), Fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetric analysis (DSC), linear sweep voltametry (LSV) and AC impedance analysis. Solid state electrochemical cell has been fabricated and cell parameters have been reported and also a single proton exchange membrane (PEM) fuel cell has been constructed and its open circuit voltage has been measured.

2. Experimental technique

2.1. Materials used

The polymer electrolyte has been prepared by solution casting technique. Iota carrageenan and ammonium nitrate have been used as the raw materials in this study.

2.2. Film casting

In this work, appropriate weight of I-carrageenan (Tokyo Chemical Industry, Japan) and NH_4NO_3 (NICE Chemicals Private Ltd., Kerala, India) have been dissolved individually in double-distilled water and these solutions have been mixed together and stirred well by using magnetic stirrer to obtain a homogeneous mixture. The obtained mixture is poured into Petri dish and is subjected for drying (60 °C for 2 days) in hot air oven. Mechanically strong, transparent and flexible films have been obtained with thickness in the range from 0.64 to 0.16 μm.

2.3. Characterization

2.3.1. Structural study

The X-ray diffraction pattern of the polymer electrolytes have been recorded at room temperature by XPERT-PRO diffractometer system using the Cukα radiation in the range of 2θ = 10° to 90°.

2.3.2. Vibrational study

The FTIR measurement has been made with a SHIMAZDU IR Affinity-1 spectrometer instrument in the wave number range of 400–4000 cm^{-1} with the resolution of 1 cm^{-1}.

2.3.3. Thermal study

The thermal stability of the polymer electrolytes have been studied using DSCQ20 V4.10 build 122 with a resolution of 0.01 mg. The films have been taken in an aluminum pan and heated up to 500 °C with the heating rate of 5 °C/min under controlled air atmosphere and the films have been purged using 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.

2.3.4. Impedance study

The ionic conductivity study of the polymer electrolytes has been carried out in the temperature range of 303–373 K over a frequency range of 42 Hz–1 MHz using a computer controlled HIOKI 3532 LCR meter.

2.3.5. Transference number measurement

The Wagner's polarization method is used to calculate the transference number of the polymer electrolyte in which, the DC current has been monitored as a function of time on application of a fixed DC voltage of 1 V across the cell SS/(I-carrageenan + NH_4NO_3)/SS. The transport parameters have been calculated from the obtained results.

2.3.6. Electrochemical stability studies

The LSV responses of I-carrageenan with NH_4NO_3 have been accomplished using Biologic Science Instruments VSP-300, France. These cells have been analyzed at a scan rate of 1 mV/s with the configuration of stainless steel (SS)/polymer electrolyte/SS in the potential range of 0–5 V.

2.3.7. Primary proton battery fabrication

Solid-state battery with configuration (Zn + $ZnSO_4 \cdot 7H_2O$ + C) (anode)/(I-carrageenan + NH_4NO_3)/(PbO_2 + C + Electrolyte + V_2O_5) (cathode) has been fabricated at ambient temperature and its discharge characteristic has been studied at ambient temperature.

Preparation of the anode desired proportions (3:1:1) of zinc (metal) powder, $ZnSO_4 \cdot 7H_2O$ and graphite powder have been taken and mixed together, and finally grind well. Then, the mixture has been pressed to form a thin pellet. Preparation of cathode the ratio of (8:2:1:0.5) PbO_2, V_2O_5, graphite and polymer electrolyte has been taken and mixed together, and finally grind well. The above mixture has been made into thin pellet. Graphite C has been added to introduce the electronic conductivity, while the addition of the polymer electrolyte helps in reducing the electrode polarization. The bio-polymer electrolyte containing (1.0 g I-carrageenan: 0.4 wt% NH_4NO_3) has been sandwiched between the anode and cathode.

2.3.8. Single-PEM fuel cell construction

Using the highest conducting bio-polymer electrolyte 1.0 g I-carrageenan: 0.4 wt% NH_4NO_3 proton exchange membrane (PEM) fuel cell has been constructed and its open circuit voltage is measured.