Solid State Ionics 224 (2012) 51–57

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

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

Chemical interaction and conductivity of carboxymethyl κ-carrageenan based green polymer electrolyte

N.N. Mobarak [a], N. Ramli [a,*], A. Ahmad [a,*,1], M.Y.A. Rahman [b,**]

[a] School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor Darul Ehsan, Malaysia
[b] College of Foundation and General Studies, Universiti Tenaga Nasional, 43009, Kajang, Selangor, Malaysia

ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form 7 June 2012
Accepted 12 July 2012
Available online 9 August 2012

Keywords:
Carrageenan
Carboxymethyl
Ionic conductivity
Green polymer electrolyte

ABSTRACT

The potential of κ-carrageenan derivatives as a green polymer electrolyte has been explored. κ-Carrageenan extracted from marine red algae was reacted with monochloacetic acid to form carboxymethyl κ-carrageenan. The powders were characterized by reflection fourier transform infrared (ATR-FTIR) spectroscopy,^{13}C nuclear magnetic resonance, ^{1}H nuclear magnetic resonance, X-ray diffraction and elemental analysis to confirm the structural, crystallinity and the degrees of substitution. A green polymer electrolyte of κ-carrageenan and carboxymethyl κ-carrageenan were prepared by solution-casting technique. The films were characterized by reflection fourier transform infrared (ATR-FTIR) spectroscopy and electrochemical impedance spectroscopy to determine the chemical interaction and ionic conductivity. The decrease in intensity of hydroxyl, carbonyl, sulfate and ether band confirmed the polymer solvent complex formation. XRD spectra show that chemical modification of κ-carrageenan does not change its amorphous properties. The ionic conductivity was found to increase by three magnitudes higher with the chemical modification of κ-carrageenan. The conductivity achieved was 2.0×10^{-4} S cm^{-1} for carboxymethyl κ-carrageenan in comparison to 5.3×10^{-7} S cm^{-1} for κ-carrageenan.

1. Introduction

Over a year, the electrochemical power was obtained by using liquid electrolyte due to its high ionic conductivity. Yet, this liquid electrolyte gives a lot of problems such as leakage, reaction with electrode, and poor electrochemical stability, which makes it unsuitable for the use in electrochemical devices. When the first reported solid polymer electrolyte was made in 1973, the researcher realized that this polymer electrolyte can be used to replace the liquid electrolyte due to its excellent mechanical and thermal stability and high ionic conductivity [1,2]. The synthetic polymers used in the making of proton-conducting polymer electrolytes are polyethylene oxide, polyacrylic acid, and polyvinyl alcohols [3] which are high-cost polymers compared to biopolymer such as carrageenan.

κ-Carrageenan is a sulfated polysaccharide extracted from *Rhodophyceae*, which is a red seaweed. The structure of κ-carrageenan consists of alternating (1→3)-α-D-galactose-4-sulfate and (1→4)-β-3, 6-anhydro-D-galactose residues joined in a linear chain. This biopolymer has been considered to be a good and environment-friendly polymer matrix [4]. The chemical structure of κ-carrageenan is shown in Fig. 1(A). However, to extend the use of κ-carrageenan, the chemical modification on it had been done in order to produce carboxymethyl κ-carrageenan. The production of carboxymethyl κ-carrageenan had attracted interests of industrial and scientific organisations in recent years. Products such as metal adsorbent, magnetic nanospheres and encapsulant for oral delivery have been developed from carboxymethyl κ-carrageenan. However, the properties of carboxymethyl κ-carrageenan, especially the ability to conduct electricity, to our knowledge, have not been studied [5]. Fig. 1(B) shows the structure of carboxymethyl κ-carrageenan.

Carrageenan can form cross-linking networks with other components in the electrolyte because of their rich hydroxyl groups in molecule structure [4]. Moreover, κ-carrageenan has oxygen atom which is important to form a coordinated bond with cations. The new derivatives of κ-carrageenan will have more number of oxygen compared to the original κ-carrageenan. It is expected to provide more vacancy for cations or proton to coordinate. Thus, this will give a high ionic conductivity compared with original κ-carrageenan. Besides that, compared to traditional polyethylene oxide polymer electrolyte, polysaccharide matrix shows much lower crystallinity at room temperature. These may increase the ionic mobility of the cations or proton and give an excellent thermal and chemical stability of green polymer electrolyte.

In this study, the potential of κ-carrageenan derivatives as a green polymer electrolyte is explored. Carboxymethyl κ-carrageenan powder which has been synthesized will be characterized by using reflection fourier transform infrared (ATR-FTIR) spectroscopy,^{13}C nuclear magnetic resonance, ^{1}H nuclear magnetic resonance, X-ray diffraction (XRD) and elemental analysis. Furthermore, carboxymethyl κ-carrageenan based

---

* Corresponding authors.
** Corresponding author. Tel.: +60 3 89287262; fax: +60 3 89263503.
E-mail addresses: naza@ukm.my (N. Ramli), azizan@ukm.my (A. Ahmad), yusri@uniten.edu.my (M.Y.A. Rahman).
[1] Tel.: +60 3 89215439; fax: +60 3 89215410.

0167-2738/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2012.07.010

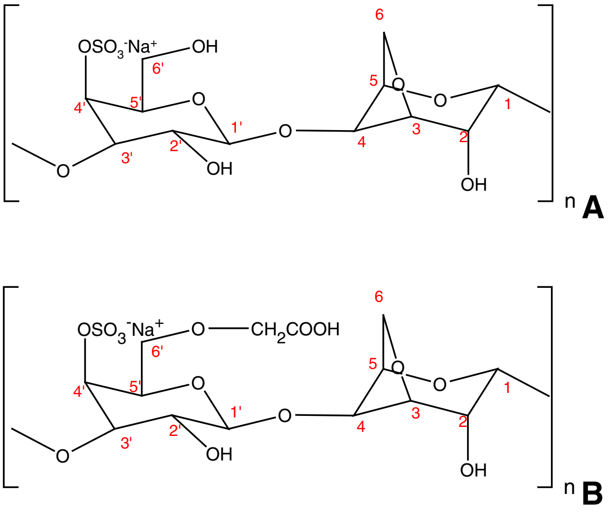

Fig. 1. The chemical structure of (A) κ-carrageenan and (B) carboxymethyl κ-carrageenan.

green polymer electrolyte which prepared via solution casting technique was characterized by using a reflection fourier transform infrared (ATR-FTIR) spectroscopy and an AC electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

κ-Carrageenan was commercially obtained from Fluka (Switzerland). The sodium hydroxide, isopropanol, and monochloroacetic acid were supplied by Sigma-Aldrich. All materials were used without further purification.

2.2. Preparation of carboxymethyl κ-carrageenan powder

Carboxymethyl κ-carrageenan was prepared according to Sun et al.'s method [6] using κ-carrageenan as precursor. κ-Carrageenan, sodium hydroxide, isopropanol and water were mixed together and alkalized at 50 °C for 1 h. Monochloroacetic acid was dissolved in isopropanol in the flask and added to the reaction mixture. It was left to stir for 4 h at 50 °C and then terminated by adding alcohol. The solid was filtered and rinsed with ethanol and vacuum dried at room temperature.

2.3. Preparation of membrane

κ-Carrageenan and carboxymethyl κ-carrageenan solutions were prepared by dissolving κ-carrageenan in a 1% (v/v) aqueous acetic acid solution. After complete dissolution, the solutions were cast in petri dishes and left to form a film. The transparent films were obtained after drying at room temperature for 72 h. The films were then transferred into a desiccator for continuous drying.

2.4. Sample characterization

ATR-FTIR analysis was carried out using Perkin Elmer Spectrum 2000 in the range of 4000 to 400 cm^{-1} with scanning resolution of 4 cm^{-1}. This analysis was conducted to observe changes of the functional group before and after modification. Besides that, it is also to examine the interaction which occurs between polymer matrix and acetic acid solution based on the changes of the functional group. ^{13}C-NMR and ^{1}H-NMR analyses were performed in order to confirm the structure of κ-carrageenan derivatives using Bruker Avance 111 600 MHz where κ-carrageenan and carboxymethyl κ-carrageenan were dissolved in the solvent D_2O [5]. Elemental analysis was carried out using Eager 300 EA 112 to determine the element content and the degrees of substitution in κ-carrageenan derivatives. X-ray diffraction model D5000 Siemens was used to carried out in order to determine the nature of the prepared samples whether amorphous, crystalline, or both. The data were collected from the range of diffraction angle 2θ from 3° to 60° at the rate 0.05°s^{-1}. The analysis was conducted at room temperature. The alternating current (AC) impedance measurement was carried out using a high frequency response analyzer (HFRA; Solartron 1260, Schlumberger) and an electrochemical interface (SI 1286) in the frequency range of 1 Hz–10 MHz with 10 mV amplitude. The polymer electrolyte was sandwiched between the stainless steel ion-blocking electrodes with a surface contact area of 2.0 cm^2. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using the Zview analyzer software. The conductivity values (σ) have been calculated from the equation $\sigma = tR_b^{-1}A^{-1}$, where t is the film thickness (cm) and A is the active area of the electrode (cm^2). The EIS analysis was performed at room temperature.

3. Result and discussion

3.1. Characterization of carboxymethyl κ-carrageenan powder by ATR-FTIR, ^{13}C-NMR and ^{1}H-NMR

The IR spectra (Fig. 2), ^{13}C-NMR (Fig. 3) and ^{1}H-NMR (Fig. 4) data of carboxymethyl κ-carrageenan and κ-carrageenan show the successful synthesis of carboxymethyl κ-carrageenan. The carboxymethylation of carrageenan employed the Williamsons's ether synthesis process, a consecutive two step reaction [7,8]. The reaction proceeds with a strong base such as sodium hydroxide that deprotonates the hydroxyl groups in κ-carrageenan to form alkoxides, thereby increasing their nucleophilicity. The carboxymethyl groups are then formed in a reaction between the carrageenan alkoxides and monochloroacetic acid. The overall reaction is shown in Scheme 1 [7].

Fig. 2 shows the infrared spectra of κ-carrageenan (A) and carboxymethyl κ-carrageenan (B) in the form of powder. Fig. 4A showed the basic characteristic of κ-carrageenan. The bands at 1261 cm^{-1} and 850 cm^{-1} were assigned respectively to O═S═O symmetric vibration and C_4–O–S to stretching vibration [5,9]. The band at 930 cm^{-1} proved the existence of C–O–C of 3,6-anhydro-D-galactose. It also displayed an absorbance band at 1159 cm^{-1} due to bridge C–O stretch [5,10]. Band around 1070 cm^{-1}, 2949 cm^{-1} and 3462 cm^{-1} was reported to be related to C–O stretch, C–H stretch and O–H

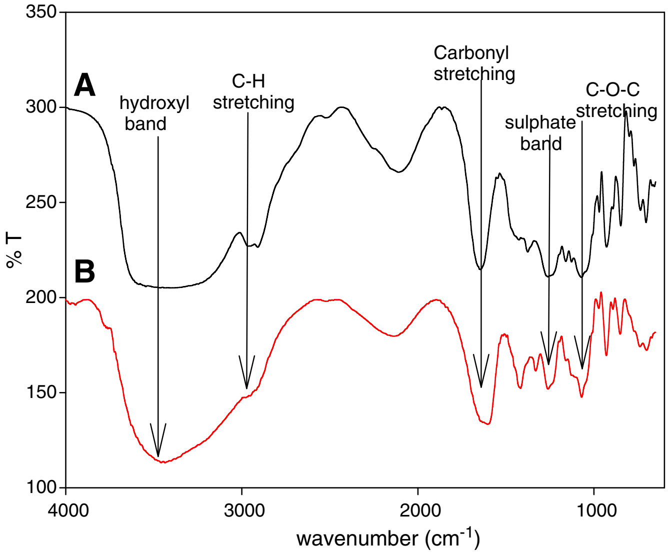

Fig. 2. FTIR spectra of powder (A) κ-carrageenan and (B) carboxymethyl κ-carrageenan.