Electrochimica Acta 92 (2013) 161–167

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Conductivity enhancement via chemical modification of chitosan based green polymer electrolyte

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ARTICLE INFO

Article history:
Received 19 September 2012
Received in revised form
23 December 2012
Accepted 29 December 2012
Available online 6 January 2013

Keywords:
Chitosan
Carboxymethyl
Ionic conductivity
Green polymer electrolyte

ABSTRACT

The potential of carboxymethyl chitosan as a green polymer electrolyte has been explored. Chitosan produced from partial deacetylation of chitin was reacted with monochloroacetic acid to form carboxymethyl chitosan. A green polymer electrolyte based chitosan and carboxymethyl chitosan was prepared by solution-casting technique. The powder and films were characterized by reflection Fourier transform infrared (ATR-FTIR) spectroscopy, ^{1}H nuclear magnetic resonance, elemental analysis and X-ray diffraction, electrochemical impedance spectroscopy, and scanning electron microscopy. The shift of wavenumber that represents hydroxyl and amine stretching confirmed the polymer solvent complex formation. The XRD spectra results show that chemical modification of chitosan has improved amorphous properties of chitosan. The ionic conductivity was found to increase by two magnitudes higher with the chemical modification of chitosan. The highest conductivity achieved was 3.6×10^{-6} S cm^{-1} for carboxymethyl chitosan at room temperature and 3.7×10^{-4} S cm^{-1} at 60 °C.

1. Introduction

The depletion of petroleum resources coupled with increasing environmental regulation are acting synergistically to provide the impetus for new materials and products that are compatible with the environment and independent of fossil fuels [1]. Nowadays, the natural polymers from marine resources such as chitin and alginate have attracted more and more attention, owing to their abundant sources, friendliness to the environment, and potential to substitute for some petrochemicals [2]. In this study, chitosan which was obtained from partial deacetylation of chitin, composing of β-(1,4)-2-amino-2-deoxy-D-glucopyranose (GLcN) and 2-acetamido-2-deoxy-D-glucopyranose (GLcNAc) residues has been used as the base polymer because it has several polar groups (OH and NH_2) in its structure [3,4]. Based on the previous studies, the conductivity of chitosan-based polymer electrolytes has been improved by complexing with lithium and ammonium salts [1,5,6], blended with different polymer such as poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) [7,8] and the addition of plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) [4]. However, the studies involving usage of chitosan derivatives are still new in the polymer electrolyte field. The chemical modification of chitosan by substituting the carboxymethyl group will enhance its conductivity leading to its use in green polymer electrolytes.

In this study, the potential of chitosan derivatives as a green polymer electrolyte has been explored. Carboxymethyl chitosan powder which was synthesized has been characterized by using reflection Fourier transform infrared (ATR-FTIR) spectroscopy, ^{1}H nuclear magnetic resonance, X-ray diffraction (XRD) and elemental analysis. Furthermore, carboxymethyl chitosan based green polymer electrolyte which was prepared via solution casting technique was characterized by using an AC electrochemical impedances spectroscopy (EIS), reflection Fourier transform infrared (ATR-FTIR) spectroscopy and scanning electron microscope (SEM).

2. Experimental

2.1. Materials

Chitosan was commercially obtained from ChitoChem. The sodium hydroxide, isopropanol, and monochloroacetic acid were purchased from Sigma–Aldrich. All materials were used without further purification.

2.2. Preparation of carboxymethyl chitosan powder

Carboxymethyl chitosan was prepared according to Sun et al.'s method [9] using chitosan as precursor. Chitosan, sodium hydroxide, isopropanol and water were mixed together and alkalized at a

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http://dx.doi.org/10.1016/j.electacta.2012.12.126

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

Chitosan and carboxymethyl chitosan solutions were prepared by dissolving chitosan in different concentration of aqueous acetic acid solution. After complete dissolution, the solutions were cast into Petri dishes and dried at room temperature until films were formed. The films were kept in desiccator for continuous drying.

2.4. Sample characterization

ATR-FTIR analysis was carried out using Perkin-Elmer Spectrum 2000 in the range of 4000–400 cm^{-1} with scanning resolution of 4 cm^{-1}. This analysis was conducted to observe changes of the functional group before and after modification interactions between polymer matrix and acetic acid solution were examined based on the changes of the peaks and functional group. ^1H NMR analyses was performed to confirm the structural of chitosan derivatives using Bruker Avance 111 600 MHz where chitosan and carboxymethyl chitosan were dissolved in the mixture of solvent between D_2O and CD_3COOD [10]. Elemental analysis was carried out using Eager 300 EA 112 to determine the element content and the degrees of substitution in chitosan derivatives. X-ray diffraction model D5000 Siemens was used to carry out to determine the amorphous and crystalline properties of the prepared samples. The data was collected in the range of diffraction angle 2θ from 3° to 35° at the rate $0.05^\circ\ s^{-1}$.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 at room temperature. The polymer electrolyte was sandwiched between the stainless steel blocking electrodes with a contact surface 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 morphologies of the polymer electrolytes were examined by SEM Philip XL 30 model.

3. Results and discussion

3.1. Characterization of carboxymethyl chitosan powder by FTIR and ^1H NMR

The synthesis of carboxymethyl chitosan powder was characterized using FTIR, ^1H NMR and elemental analysis. The carboxymethylation of chitosan was employed by Williamsons's ether synthesis process; a consecutive two-step reaction [11,12]. Fig. 1A shows the FTIR spectra of chitosan. The main characteristic peaks of chitosan are at 3291 (O—H stretch), 2876 (C—H stretch), 1637 ($C(O)—CH_3$), 1578 (N—H bend), 1148 (bridge O stretch), and 1056 cm^{-1} (C—O stretch). Chitosan powder (Fig. 1A) absorption was at 1578 cm^{-1} ascribed the N—H bending vibration mode of non-acylated α-aminoglucose primary amines, and a very weak absorption at 1637 cm^{-1} due to the presence of the acetylated groups [13]. However, after the substitution of carboxymethyl group on chitosan, the spectrum changed (Fig. 1B). Specifically, the intensity of the absorption peaks at 1588 cm^{-1} and 1426 cm^{-1} which corresponded the carboxyl group overlapping with N—H bend and $—CH_2COONa$ group increased, which indicated the substitution of carboxymethyl group on chitosan [14,15]. In addition, the peak intensity around 1331 cm^{-1} of Fig. 1C increased obviously. This proved the quantity of —C—O stretch increased as carboxymethyl group substituted on hydroxyl group [10]. Besides that, the carboxymethylation of chitosan proved by the existence of new peak at 2912 cm^{-1} corresponded to the asymmetric stretching vibration of methylene group in $—CH_2COONa$. In this research, the carboxymethylation of chitosan was not further with the addition of hydrochloric acid. Therefore there are no bands at 1730 cm^{-1} which corresponding to the —COOH [14,16].

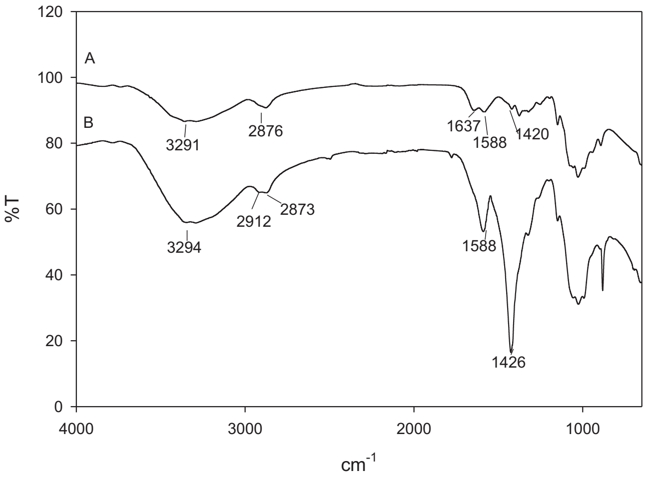

Fig. 1. FTIR spectra of powder (A) chitosan and (B) carboxymethyl chitosan.

Fig. 2 shows the ^1H NMR spectra of carboxymethyl chitosan. The proton assignment of carboxymethyl chitosan as follows (ppm): 2.01 (H7), 3.12 (H2), 3.69 (CH, carbon of glucosamine ring with the substituted amino group), 3.7–4.0 (H3, H4, H6), 4.17 (H8a), 4.66 (H5), 4.93 (H1) [17]. The appearance of the small proton signal at 3.4 ppm was due to mono-substitution of the amino groups of chitosan, which indicated that less than 10% of chitosan amino groups were also carboxymethylated during the occurrence of O-carboxymethylation as reported by the previous reports [17,18].

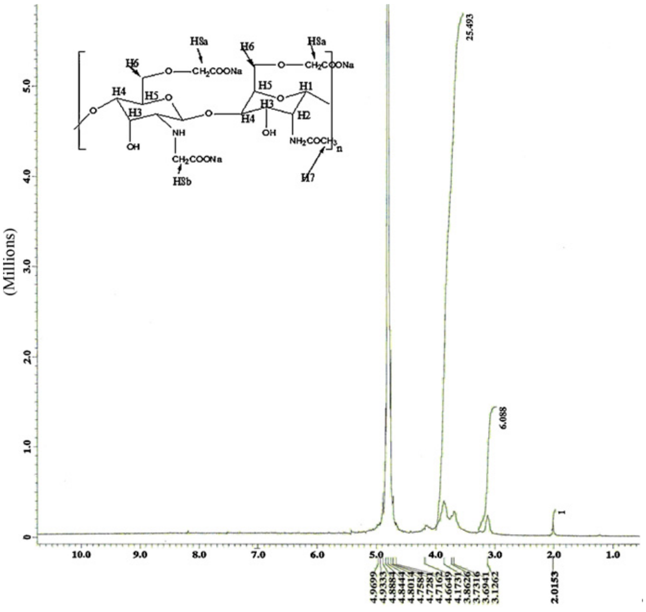

Fig. 2. ^1H NMR spectra of carboxymethyl chitosan powder.