Makara J. Technol. 23/1 (2019), 48-52
doi: 10.7454/mst.v23i1.3643

Electrical Properties of A Novel Solid Biopolymer Electrolyte based on Alginate Incorporated with Citric Acid

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Abstract

In the present study, a novel solid biopolymer electrolyte (SBE) system is introduced by doping citric acid into alginate polymer. A sample of the alginate-citric acid SBE system was prepared via a solution casting technique. Using electrical impedance spectroscopy (EIS), the electrolytes of alginate-citric acid analyzed from 5 Hz to 1 MHz achieved the highest conductivity at 20 wt.% of 5.49×10^{-7} S cm^{-1}. The temperature dependence of various citric acid amounts obeyed the Arrhenius rule with R^2~1, where all SBE systems were thermally activated with increasing temperature. The dielectric studies of the alginate-citric acid SBE system showed non-Debye behavior based on data measured using complex permittivity (ε*) and complex electrical modulus (M*) at selected temperature, where no single relation was found in the new biopolymer electrolyte system.

Abstract

Karakterisasi Sifat-Sifat Listrik pada Alginat Berbasis Elektrolit Biopolimer Padat Baru yang Dimasukkan dengan Asam Sitrat. Di dalam studi kali ini, suatu sistem elektrolit biopolimer padat (SBE) baru telah diperkenalkan dengan mendoping asam sitrat ke dalam polimer alginat. Sampel sistem SBE alginat-asam sitrat dibuat melalui teknik pengecoran larutan. Dengan menggunakan Spektroskopi Impedansi Listrik (Electrical Impedance Spectroscopy (EIS)), elektrolit-elektrolit alginat-asam sitrat telah dianalisis dari 5 Hz sampai 1 MHz mencapai nilai konduktivitas tertinggi pada 20% berat sebesar 5,49 x 10-7 S cm-1. Ketergantungan temperatur berbagai komposisi asam sitrat terbukti mentaati aturan Arrhenius dengan R2~1 di mana semua sistem SBE diaktifkan secara termal ketika menaikkan temperatur. Studi-studi dielektrik tentang sistem SBE alginat-asam sitrat menunjukkan suatu perilaku non-debye berdasarkan pada data yang diukur dengan menggunakan permitivitas kompleks (ε*) dan modulus listrik kompleks (M*) pada temperatur yang dipilih di mana tidak ditemukan adanya hubungan tunggal di dalam sistem elektrolit biopolimer baru.

Keywords: biopolymer; ionic conductivity; Arrhenius; dielectric studies

1. Introduction

In recent years, electrolytes have been widely used in electrochemical industry in such applications as batteries, supercapacitors, solar cells, fuel cells and monochromic devices. This study introduces the development of electrolyte using a biopolymer material. Most biopolymers (natural polymers) are biodegradable, low cost, low toxicity, eco-friendly and abundant compared to current electrolyte systems that mostly use hazardous heavy-metal such as lead, lithium and mercury. Previous research has shown that biopolymers can achieve good conductivity, including polymer electrolyte (PE) systems of carboxyl methylcellulose (CMC) [1], chitosan [2], starch [3], cornstarch [4], and carrageenan [5].

Alginate biopolymer has good potential as a backbone polymer matrix in a solid biopolymer electrolyte (SBE) system. Pure alginate is extracted from cell walls of brown algae with the empirical formula $NaC_6H_7O_7$ [6],[7]. In industry, the biocompatible and low cost alginate biopolymer produces good thickeners, stabilizers, film-formers and gel-formers with the possibility to commercialize around the world [8, 9]. Alginate is suitable as a host polymer but it has low conductivity. Therefore, a dopant system is needed to enhance the ionic conductivity performance.

In proton-based conductive electrolytes, citric acid (CA) acts as a dopant with antioxidant, buffering, chelating activities and good water solubility [10]. CA has been used widely in industrial areas, such as the food, textile, pharmaceutical and chemical industries, because of its dual function as a stabilizing and reducing agent [11]. CA is well known for its function as a dopant that consists of three-carboxyl anions, which easily adsorb to a surface polymer and can exert either hydrophobic or coulombic effects on alginate [12].

In the present study, a protonic conductive SBE system based on alginate doped with CA at various concentrations was prepared using a solution casting technique. The conductivity and dielectric behavior of the alginate-CA based SBE system were measured and characterized using electrical impedance spectroscopy (EIS).

2. Methods

Preparation of the SBE system An SBE based on alginate doped with citric acid (CA) was prepared using a solution casting technique. 2 g of alginate (Shaanxi Orient Co.) powder was dissolved in 98 mL distilled water and doped with different concentrations of CA (5–30 wt.%). The alginate-CA was magnetically stirred until a homogenous solution was obtained. The solution was cast into Petri dishes and left to dry in the oven until a thin film formed completely. The film was further dried in desiccators filled with silica gel to remove the solvent. The concentration of CA and designation of the SBE systems are shown in Table 1.

Characterization of the SBE system EIS was used to determine the conduction properties of the system using a HIOKI 3532-50 LCR Hi-Tester from 303–353 K with frequencies ranging from 50 Hz to 1 MHz. The alginate-CA films were cut to a suitable size with surface area as previously reported [13]. The thickness of the SBE system, t was measured using a digital thickness gauge (DML3032). The ionic conductivity of the alginate-CA SBE system was calculated using the following equation:

Table 1. Designation for the Alginate-CA SBE Systems

Sample	Designation	CA concentration (wt.%)
1	AlCA-0	0
2	AlCA-1	5
3	AlCA-2	10
4	AlCA-3	15
5	AlCA-4	20
6	AlCA-5	25
7	AlCA-6	30

$$\sigma = \frac{l}{R_b A} \tag{1}$$

where l is the thickness of the electrolytes, A is the contact area (cm^2) and R_b is the bulk resistance of the SBE system obtained from the Nyquist plot.

Dielectric study The dielectric constant, ε_r is also called the total charge stored in the material while the dielectric loss, ε_i is the loss of energy.

The dielectric constant and dielectric loss are calculated using the following equations:

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \tag{2}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \tag{3}$$

Modulus study The real modulus, M_r and imaginary modulus, M_i were calculated using the following equations:

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \tag{5}$$

$$M_i = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \tag{6}$$

3. Results and Discussion

Conductivity study The alginate-CA of the SBE system was analyzed at ambient temperature, 303 K. Figure 1 depicts the ionic conductivity of different CA concentrations incorporated into alginate polymer at ambient temperature. The ionic conductivity was increased from 5.51 × 10^{-8} S cm^{-1} for AlCA-0 to an optimum value at 5.49 × 10^{-7} S cm^{-1} for AlCA-4. The change in ionic conductivity with the addition of CA was due to the complexation between alginate and CA where high dispersion of H$^+$ ions occurred and the ionic mobility also increased rapidly [14, 15]. The ionic conductivity started to decrease when CA was greater than 20 wt. %. According to Othman and Isa [16], the decrease in ionic conductivity after AlCA-4 was due to neutral aggregation of the re-associated ions, leading to formation of an ion cluster.

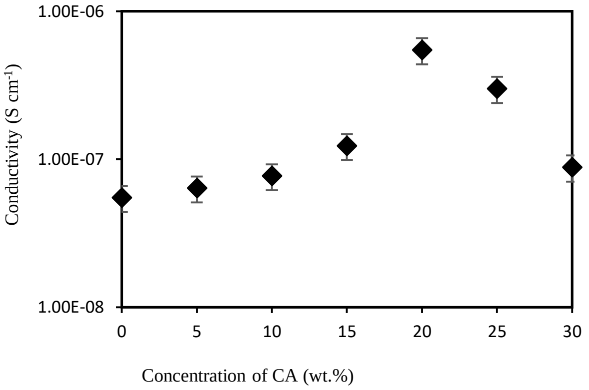

Figure 1. Ionic Conductivity of the Alginate-CA SBE Systems at Ambient Temperature

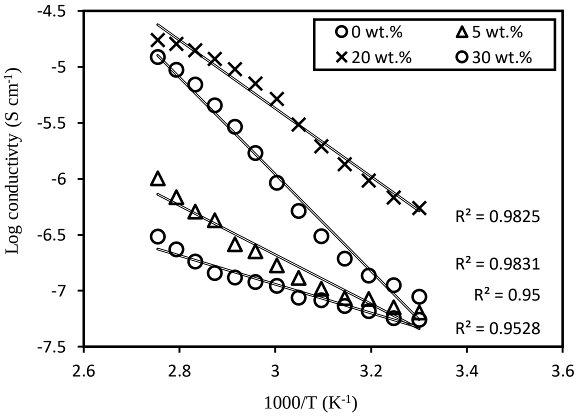

Figure 2. Temperature Dependence of the Alginate-CA of SBE System

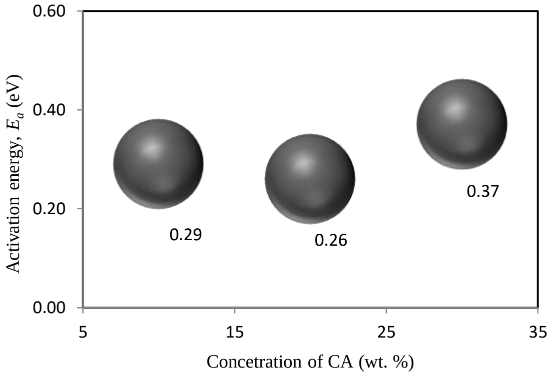

Figure 3. Activation Energy for the Alginate-CA SBE Systems

Figure 2 shows the log conductivity versus 1000/T for different concentrations of CA from 303 K to 363 K. AlCA-4 had greater conductivity than the other systems. The temperature dependent study of the SBE system obeys the Arrhenius relationship, where the regression value, R^2, is in the range of 0.95 to 0.99 [17], [18]. The promising ionic conductivity indicates that alginate can also host proton (H^+) conduction as well as other polymers to be used in an electrolyte system. As shown in Figure 2, the conductivity-temperature data obeys Arrhenius behaviour, where the nature of the cation transport is quite similar to that in ionic crystals; the ions migrate into nearer vacant sites and enhance the ionic conductivity [19]. Therefore, the activation energy, E_a was calculated using the Arrhenius equation:

$$\sigma = \sigma_0 \, exp\left(-\frac{E_a}{kT}\right) \tag{7}$$

where E_a is the activation energy, σ is the conductivity of the SBE system, σ_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the temperature in Kelvin.

The activation energy, E_a is calculated from a linear fit of the temperature dependence study and calculated using Equation (7). The activation energy, E_a is the minimum energy needed for an H^+ ion to jump from one site to a neighbouring site due to the defect formation [20]. Figure 3 depicts the highest conductivity alginate-CA SBE system led to a decrease in E_a value (0.26 eV). The lowest E_a indicates that H^+ ions require less energy to migrate from the carbonyl group to the polymer backbone, which will enhance the ionic mobility [21].

Dielectric study Figures 4 and 5 show the study of the dielectric constant and dielectric loss for different acid concentrations at ambient temperature. At low frequency, the dielectric constant and dielectric loss increase sharply, indicating that the effect of electrode polarization and space charge occurred, confirming the non-Debye behaviour state with non-exponential relaxation in time [22]. At high frequency, the periodic reversal movement of the electric field performs rapidly, where there is no excess ion diffusion and dispersed energy in the path of the field [23]. Based on this study, there were no appreciable relaxation peaks in the frequency range. Figure 6 shows that increasing the temperature of the highest conductivity sample (AlCA-4) enhanced the dielectric value, which indicate the re-diffusion of ions where it began to aggregate, resulting in the increase in ions [24].

Modulus study Dielectric modulus is a study to approach the dielectric relaxation behavior by suppressing electrodes' polarization effect [25]. Figure 7 (a) and (b) shows the real and imaginary modulus of different CA concentrations at ambient temperature.

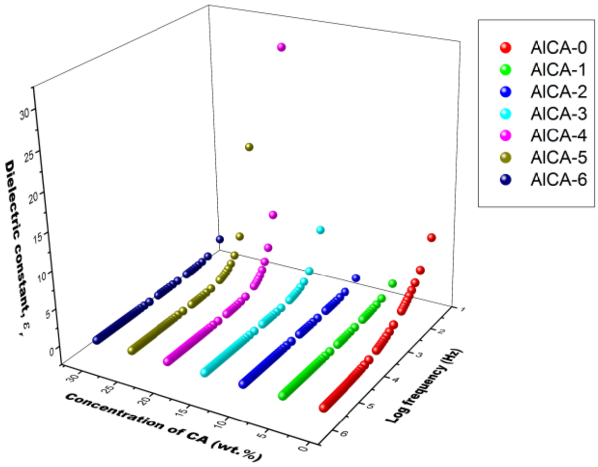

Figure 4. Dielectric Constant for the Alginate-CA SBE Systems at Ambient Temperature

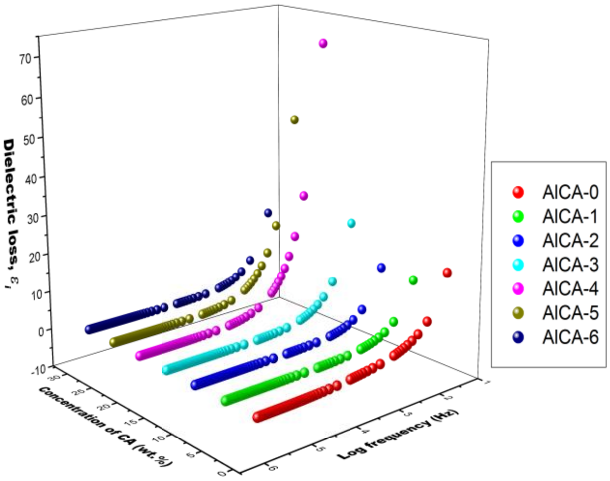

Figure 5. Dielectric Loss for the Alginate-CA SBE Systems at Ambient Temperature

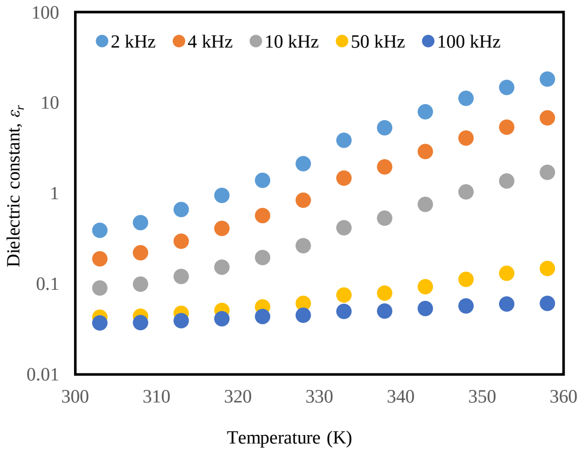

Figure 6. Dielectric Constant for the AlCA-4 SBE System

At low frequency, both Figure 7 (a) and (b) demonstrate that the M_r and M_i value approaches nearly zero. The long tail at lower frequency indicated a large capacitance associated with removal of the electrode polarization effects and a non-Debye behaviour of the alginate-CA system is confirmed [26]. At higher frequency, AlCA-4 obtained a lower real and imaginary part modulus curve. From Figure 7, all SBE systems showed peaks in the electrical modulus formalism with ionic conduction at higher frequencies [15].

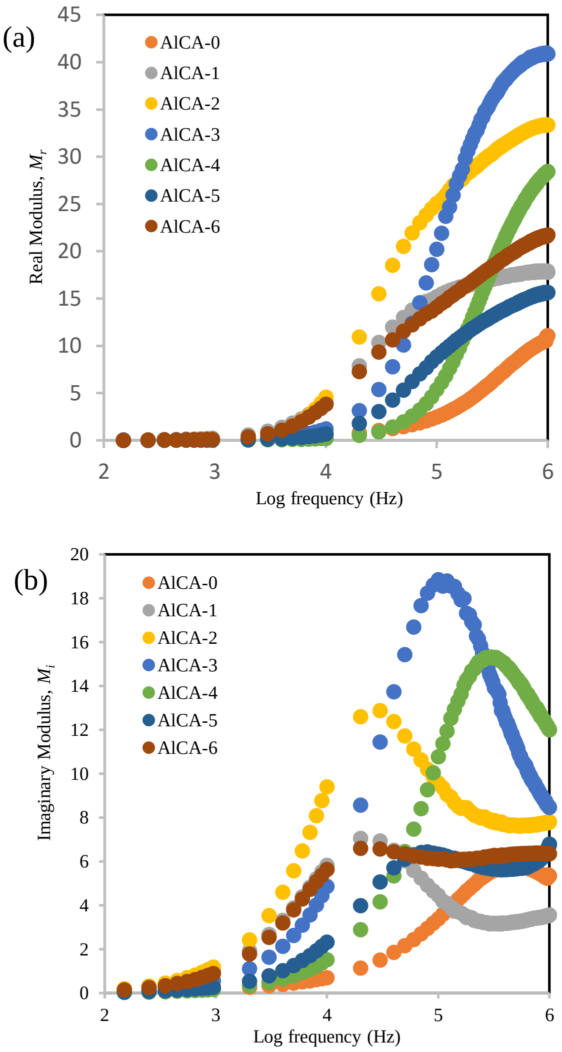

Figure 7. Frequency Dependence of (a) Real Modulus and (b) Imaginary Modulus for the Alginate-CA SBE Systems at Ambient Temperature

4. Conclusions

Various citric acid compositions using a solid biopolymer electrolyte (SBE) system based on alginate were successfully prepared using a casting technique. The optimum composition for the highest conducting sample was 20 wt.% for 5.49 × 10^{-7} S cm^{-1} at 303 K. Temperature dependence for the alginate-CA SBE system shows that the ionic conductivity exhibited Arrhenius behavior. The activation energy was inversely proportional to the ionic conductivity of the SBE system, where the highest conducting sample required a smaller E_a for the transportation of ions. The dielectric behavior of the acidic dopant systems confirmed that the conductivity followed the ionic mobility, suggesting that all SBE systems exhibit non-Debye behavior where non-single relaxation of ions were observed.

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