

THE EFFECT OF IONIC CHARGE CARRIERS IN 2-HYDROXYETHYL CELLULOSE SOLID BIOPOLYMER ELECTROLYTES DOPED GLYCOLIC ACID VIA FTIR-DECONVOLUTION TECHNIQUE

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Abstract: The Fourier transform infrared (FTIR) spectrum of each 2-hydroxyethyl cellulose (2HEC) doped with glycolic acid (GA) solid biopolymer electrolytes (SBE) sample has been deconvoluted in the wavenumber region between 1390 and 1490 cm^{-1} in order to predict the percentage of free and contact ions in the samples. Through solution casting method, 2HEC was complexed with different composition of GA and sample with 40 wt. % GA achieved the highest ionic conductivity at room temperature of $4.01 \times 10^{-4} \text{ S cm}^{-1}$, two magnitude orders higher relative to the parent host polymer. The FTIR of carboxyl stretching mode is deconvoluted, representing bands of free ions, contact ion pairs and ion aggregates to obtain an insight on ion associations. The results show that the number of free ions increases and attain maximum at 40 wt. % GA. The correspondence between free ions, contact ion pair, ion aggregates and conductivity is obvious. The increase in ion dissociation improves conductivity, while the formation of contact ion pair and ion aggregates reduces conductivity. From Transference Number Measurement (TNM), the calculated ionic species of the 2HEC-GA complexed system is confirmed predominant cationic.

Keywords: Solid biopolymer electrolytes, 2-hydroxyethyl cellulose, conductivity, FTIR-deconvolution.

Introduction

Batteries consist of three main components; anode, cathode and electrolyte. Electrolyte is the key component to the battery and it consists of free ions which behave as an electrically conductive medium. They generally consist of ions in solution, but molten and solid electrolytes are also possible, which both are developed in resolving the problems encountered in conventional liquid electrolyte battery systems such as leakage, difficulty in manufacturing, corrosive properties towards container and sealants, low power to weight ratio and limited shelf life (Freitas *et al.*, 2008; Kadir *et al.*, 2011; Aziz & Abidin, 2013). To form an electrolyte, dopant needs to be added into solvent such as water. Upon the solvation of salt, the individual atomic components are separated by the force applied in a process called chemical dissociation in which the solution applied force to hold the

ions apart (Chai & Isa, 2013; Rudhziah *et al.*, 2014). The present of freely mobile ions gives rise to the conductive behavior of the system.

The functionality of polymer electrolyte depends on an array of coupled transport phenomena that determine the conduction behavior of the system (Majid & Arof, 2005). One of the main roles of polymer electrolytes is to transport proton from anode to cathode which may then be interpreted in term of conductivity, the fundamental properties of polymer electrolyte. Transport properties of polymer electrolytes are closely related to the conduction behavior of the system (Rajendran *et al.*, 2007; Su'ait *et al.*, 2009; Ramly *et al.*, 2011). The parameter in transport mechanisms studies, supply appropriate information relating to transport and conductivity properties (Samsudin & Isa, 2012). These include number density of mobile ions, mobility of charged carriers and

diffusion coefficient. Transport properties of the polymer are important in order to assess the performance of the system and to suggest ways for improvement. Thus in this work, transport parameters of 2HEC-GA system are studied to correlate the effect of those parameters with conductivity of the system. The dependencies of all investigated parameters related to these SBEs are discussed in this work.

Method

Sample Preparation

2-hydroxyethyl cellulose (2HEC) based SBEs were prepared using solution casting technique following work done by (Samsudin *et al.*, 2014; Chai & Isa, 2016). 2 g of 2HEC with (99% purity from Sigma Aldrich) was dissolved in 100 ml distilled water at ambient temperature. Glycolic acid (GA) (99% purity from Sigma Aldrich) varied from 10 to 50 weight percent (wt.%) with 10 wt.% increment was added to the solution and stirred continuously until homogeneous. The mixtures were then casted into Petri dishes and dried in an oven at a constant temperature of 60 °C for the biopolymer films to form. The prepared samples were then peeled from Petri dishes and transported into the desiccators before further analyzed.

Characterization

The SBEs were characterized by several techniques in order to determine the behavior of the 2HEC based biopolymer electrolytes.

Electrical Impedance spectroscopy (EIS) was performed by using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer in frequency ranges of 50 to 1M Hz. The sample was cut into round pieces of films with 2 cm diameter and mounted on the holder of stainless steel electrodes which connected to the LCR tester and placed in an oven (Mettler) for temperature control purposes. The software controlling the measurement recorded and gave

a plot of real, (Z_r) and negative imaginary, ($-Z_i$) impedance for conductivity measurement. The ionic conductivity (σ) can be calculated from Eq. 1.

$$\sigma = t / (R_b A). \quad (1)$$

where, t is the thickness of electrolyte (cm), R_b is bulk impedance (Ω) from plot of $-Z_i$ versus Z_r and A is the electrode-electrolyte contact area (cm²).

Fourier Transform Infrared spectroscopy (FTIR) was carried out using Thermo Nicolet Avatar 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory with germanium crystal in the frequency range of 4000 to 700 cm⁻¹ with spectra resolution of 4 cm⁻¹. This measurement was done in confirming the complexation of polymer host, the present of specific functional groups and free ion, and proposition of conduction mechanisms. From FTIR deconvolution, number density (n), ionic mobility (μ) and diffusion coefficient (D) of charges carriers were calculated following Eq. 2 to Eq. 4.

$$n = \frac{M \times N_A}{V_{Total}} \times (\% \text{ of free ion}) \quad (2)$$

$$\mu = \frac{\sigma}{ne} \quad (3)$$

$$D = \frac{\mu kT}{e} \quad (4)$$

In Eq. 2, M is the number of moles of salt used in each electrolyte, N_A is Avogadro's number (6.02x10²³ mol⁻¹) and V_{TOTAL} is the total volume of the SBEs. In Eq. 3, e is the elementary charge (1.602x10⁻¹⁹ C) while k and t in Eq. 4, is a Boltzmann constant (1.38x10⁻²³ JK⁻¹) and absolute temperature respectively.

Transference Number Measurement (TNM) was performed to evaluate the ionic diffusion effect on the conductivity behavior of the system by means of dc polarization method (Nik Aziz *et al.*, 2010). The dc current as a function of time was monitored on application of a fixed dc voltage (1.5 V) across the sample

mounted between two stainless steel electrodes.

The ionic transference number, t_{ion} calculated from the plot of normalized polarization current with time following Eq. 5 (Samsudin *et al.*, 2014).

$$t_{ion} = \frac{I_{ion}}{I_0} \quad (5)$$

Here, I_0 is the initial current of the normalized polarization current. Knowing the value of t_{ion} , the anionic and cationic mobility (μ_-, μ_+) and diffusion coefficient (D_-, D_+) of the sample can be calculated according to the following equations (Samsudin *et al.*, 2014; Chai & Isa, 2016):

$$D = D_+ + D_- = \frac{kT\sigma}{ne^2} \quad (6)$$

$$t_+ = \frac{D_+}{D_+ + D_-} \quad (7)$$

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{ne} \quad (8)$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \quad (9)$$

Result and Discussion

Conductivity Study

Performance of SBEs can be specified by the dependency of ionic conductivity to several factors. These factors include the influences of conduction species, either's anionic or cationic types, salt composition, temperature, etc (Hirankumar *et al.*, 2004). The dependency of ionic conductivity toward salt composition provides information on the specific interaction between salt and polymer host. A typical conductivity plots for samples with various GA composition at ambient temperature is shown in Figure 1.

From Figure 1, it is observed that the ionic conductivity value of 2HEC-GA

SBEs lies between 1.15×10^{-5} to 4.01×10^{-4} S cm^{-1} . The dopant free sample has the lowest room temperature conductivity of 3.43×10^{-6} S cm^{-1} . Introducing of 10 wt.% GA into the system caused the increment of ionic conductivity about one magnitude order to 1.15×10^{-5} S cm^{-1} . The conductivity of the polymer electrolytes gradually increased with increasing GA composition and the highest was recorded for the sample with 40 wt.% GA (GA40) which is 4.01×10^{-4} S cm^{-1} , increment of two magnitude order than conductivity of parent host polymer. An increase, in ionic conductivity with dopant composition is due to the decrease of bulk resistance in the system which also reported by (Samsudin *et al.*, 2014; Chai & Isa, 2016). Increases of mobile charges provided by dissociation of ionic dopant explained the conductivity enhancement of the system by the addition of GA. However, the conductivity is observed to decreased upon addition of 50 wt.% GA. Decrement of ionic conductivity at higher dopant concentration is mainly due to the overcrowded of ion which leads to the ion clouds formation phenomenon (Chai & Isa, 2016). The formation of ion cloud is expected to limit the mobility of ions further gives limitation on the ionic conductivity which can be proven further in this work.

FTIR Deconvolution

FTIR spectroscopy is an analytical technique used for the study of structural changes in electrolytes. It was performed for further understanding on the ionic conductivity (σ) and its relationship with number density of mobile ion (n), ionic mobility (μ) and diffusion coefficient (D).

FTIR deconvolution is the process of compensating for the intrinsic line widths of bands in order to resolve possible overlapping bands (Kauppinen *et al.*, 1981). This technique yields spectra that have much narrower bands and is able to distinguish closely space features. Performing this technique allows the determination of appreciable peaks which may

then be distinguished into free or contact ions. The deconvolution was based on the Gaussian-Lorentz function using Origin fitting software (Chai & Isa, 2016). All the deconvoluted peaks fit the original spectrum with regression value approximately unity ($R^2=0.9998$).

Based on the report by (Hay & Myneni, 2007), the symmetric vibrational bands of carboxylate anion ($\nu_s\text{COO}^-$) can be observed at 1430 cm^{-1} . Hence, the bands between 1390 to 1490 cm^{-1} was deconvoluted since the bands representing the free ion are within this region. Figure 2, illustrates the deconvolution of FTIR spectra in the absorbance mode for 2HEC-GA SBEs, in a range of 1390 to 1490 cm^{-1} .

Peak at 1430 cm^{-1} was assigned to free ion attributed from GA. This peak reflects the role of cation (H^+) which attributed from carboxyl (COOH) group of GA. The dissociation of GA gives hydrogen (H^+) and glycolate ($\text{CH}_2\text{OHCOO}^-$) ions as cationic and anionic products, thus assisting ionic conduction of the systems. From Figure 2, peak located at 1407 cm^{-1} can be assigned to contact ion peak while peak at 1465 cm^{-1} are CH characteristic

band peak of 2HEC host polymer (El-Sheikh *et al.*, 2013). The area percentages of free and contact ions can be respectively calculated from the ratio of the area of free or contact ions to the total area of free and contact ions peaks (Rahman *et al.*, 2014).

Table 1 lists the percentage of free and contact ions of 2HEC-GA SBEs. It is observed that the percentage of free ion increased up to the sample GA40 due to the increases of ion dissociation, hence assisting more ion conduction. Beyond this optimum value, the percentage of free ion is observed to drop, attributed from the association of the ions (Rahman *et al.*, 2014). This result supported the reduction in ionic conductivity as discussed previously.

From percentage of free ions with respect to the composition of GA obtained from FTIR deconvolution, number density (n), ionic mobility (μ) and diffusion coefficient (D) of charges carriers were calculated following Eq. 2 to Eq. 4. Analyzing these parameter brought in deep understanding of ionic conduction behavior of the electrolytes (Arof *et al.*, 2014).

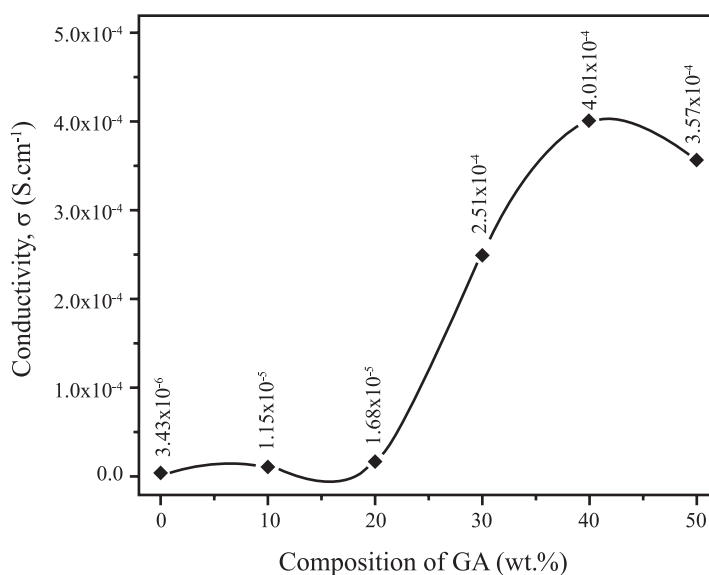


Figure 1: The conductivity of 2HEC-GA SBEs at room temperature.

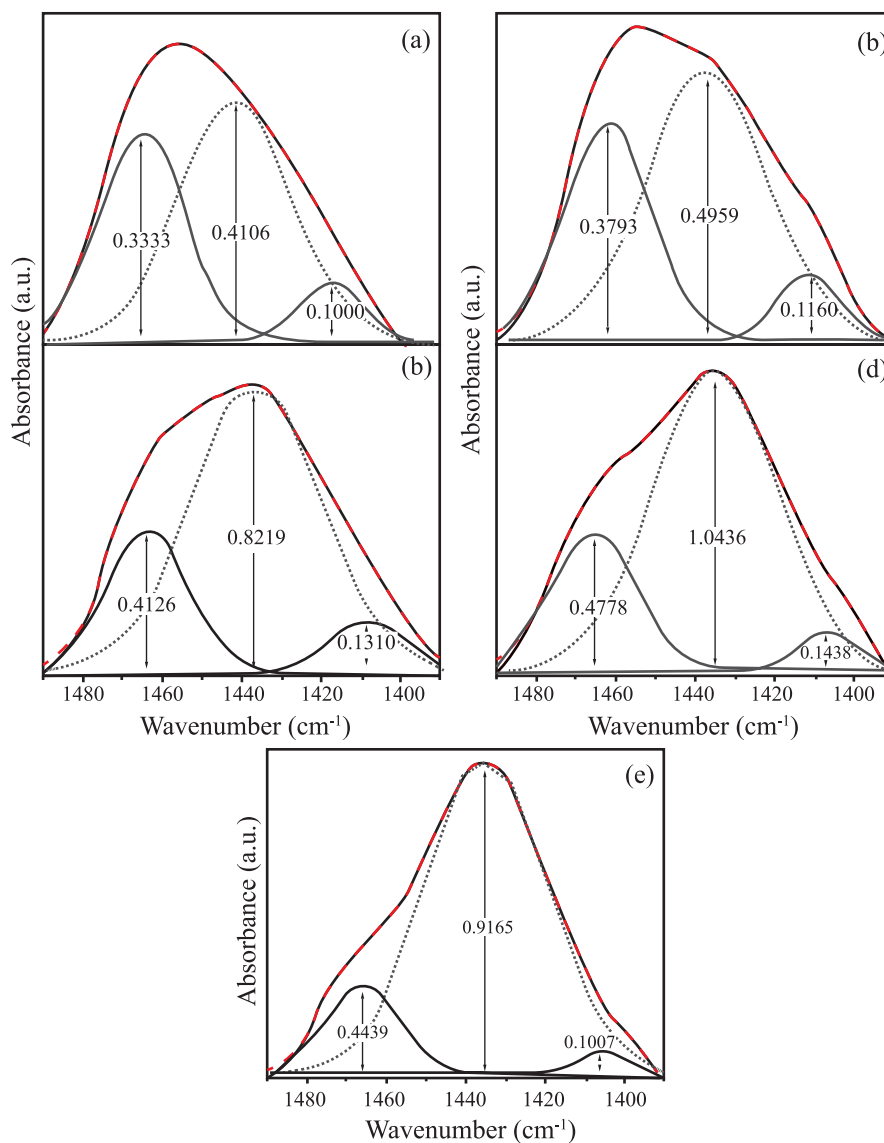


Figure 2: FTIR deconvolution of 2HEC-GA SBEs in range of 1390 to 1490 cm^{-1} .

Table 1: Percentage area of free and contact ion of 2HEC-GA SBEs

Sample	Free ion (%)	Contact ion (%)
GA10	88.24	11.76
GA20	90.00	10.00
GA30	91.67	8.33
GA40	95.45	4.55
GA50	79.31	20.69

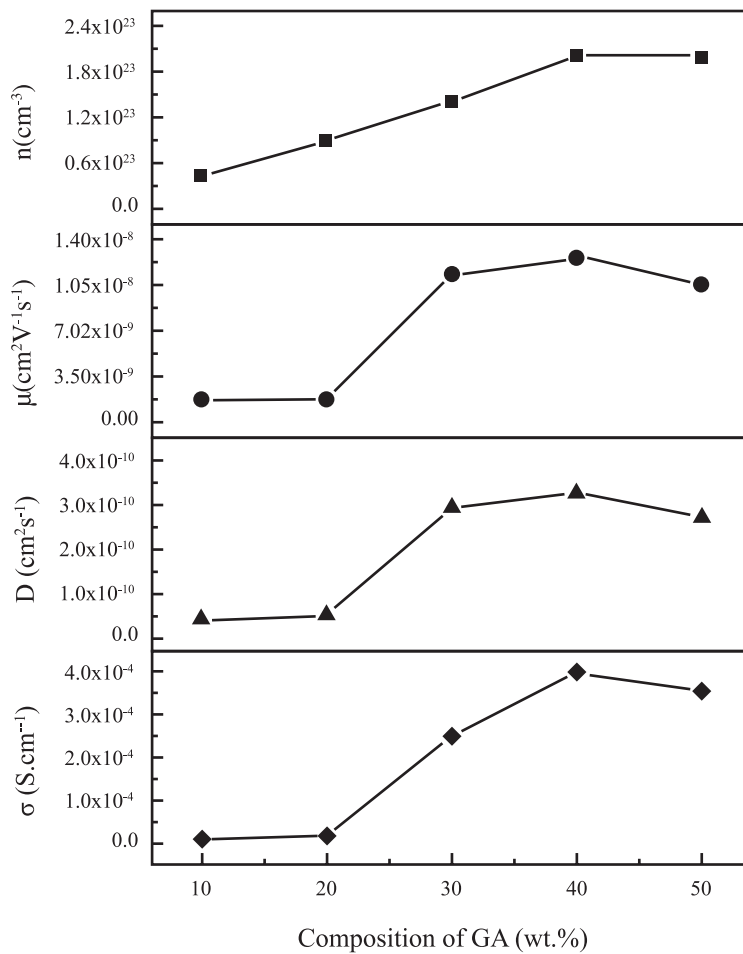


Figure 3: Variation in number density (n), mobility (μ) and diffusivity (D) of charge carriers with different GA composition

The variation of n , μ and D for every sample are shown in Figure 3. Addition of GA into the system causes the increment of number density of mobile ions in the polymer electrolytes. In this system, it is believed that doping the parental host polymer resulted in more free ions that can contribute to ionic conductivity.

From Figure 3, it can be observed that conductivity variation of 2HEC-GA SBEs is strongly dependent by the values of n , μ and D , and . Hence, it is believed that, doping 2-HEC based polymer host with GA provides more dissociated ions (H^+) to the system, thus resulting in an increasing number density of mobile ions which also influenced by the increases in ionic mobility and the diffusion coefficient of the system.

However, for sample with the highest GA composition, GA50, the number density of mobile ion (n) decreases, attributed to the formation of ion clouds where most of free ions present in the sample are blocked by the overcrowding phenomenon which in turn causes a decrement in mobility, (μ) and diffusivity, (D) of charges carriers.

Transport Study

Transference Number Measurement (TNM) was performed to further prove the effect of ionic mobility and diffusion coefficient to the conductivity behavior of electrolytes, hence classify the conducting species of SBEs (Samsudin *et al.*, 2014). As the electron conduction of SBEs can be neglected (Linford, 1988), the polarization current measurement should give the cationic transference value. Figure 4 shows the plot of polarized current versus time. It is observed that, the initial total current decreases with time due to the depletion of the ionic species and become constant at the fully depleted situation. Thus the ions were completely polarized.

From Figure 5, it can be observed that the cationic mobility and diffusion coefficient is higher than the anionic values. The ionic and electron transference number of the highest ionic conductivity sample, GA40, was found to be 0.87 and 0.13 respectively. This result clearly revealed that the charges transport in 2HEC-GA SBEs is predominantly ionic. Hence, 2HEC-GA SBEs can be said as proton conductor system with H^+ as a charge carrier.

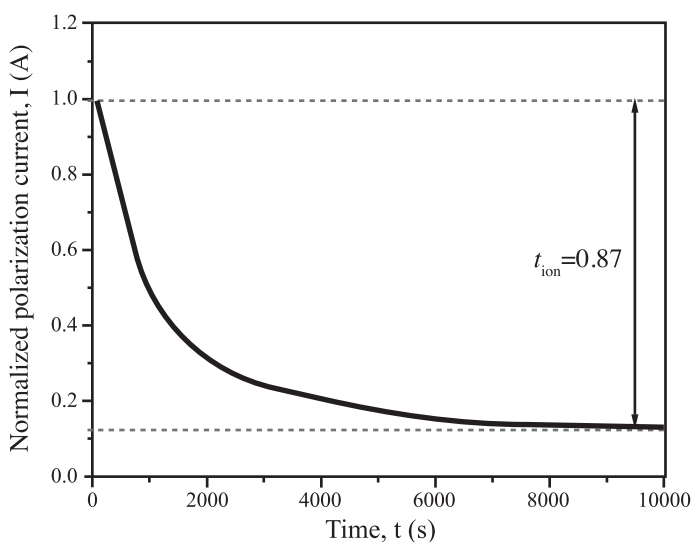


Figure 4: Polarized current versus time for sample GA40

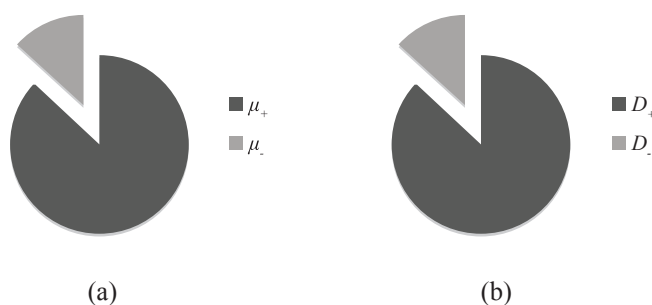


Figure 5: Anionic and cationic (a) mobility and (b) diffusivity of GA40

Conclusion

2HEC-GA solid biopolymer electrolytes have been successfully prepared by solution casting technique. Sample with 40 wt.% GA was found to have the highest ionic conductivity of $4.01 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature (30°C), increment of two magnitude order than parents host polymer. FTIR deconvolution carried out to determine the percent dissociation of free ion (H^+) from carbonyl group of GA, confirmed the dependency of ionic conductivity on the number of mobile ion (n), mobility (μ) and diffusivity (D) of the SBEs. The cationic mobility and diffusivity (μ_+, D_+) is found to be higher than anionic one (μ_-, D_-). Thus the result proved that the 2HEC-GA SBEs are proton conductor with hydrogen ion as charged carriers.

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