Ionic Conductivity and Structural Analysis of 2-hyroxyethyl Cellulose Doped with Glycolic Acid Solid Biopolymer Electrolytes for Solid Proton Battery

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Abstract. Cellulose derivatives have high potential for use as solid biopolymer electrolytes in proton batteries because they are biodegradable, affordable, have good mechanical properties and their ionic conductivity can be enhanced with addition of ionic dopant. In this work, we developed a new type of solid biopolymer electrolytes (SBEs) based on 2-hydroxyethyl cellulose (2HEC) doped with glycolic acid (GA) as an ionic dopant. A solution casting technique was used to prepare the SBEs. The ionic conductivity and structural properties of the SBEs were analysed using Electrical Impedance Spectroscopy (EIS), Fourier Transform Infrared spectroscopy (FTIR) and an X-ray Diffractometer (XRD). The highest ionic conductivity achieved was 3.80 $\times 10^{-4}$ S cm^{-1} for the sample with 40 wt.% GA concentration at room temperature. FT-IR analysis showed that complexation occurred in the polymer system from the shifting of υC-O and υ_sCOO^{-} band of 2HEC and GA. FTIR deconvolution revealed the increasing pattern of percentage free mobile ions with the addition of GA concentration until 40 wt.% GA , which can be related to the high ionic conductivity of the sample. In XRD analysis, all SBEs shows amorphous nature. Based on the results obtained, GA is a good ionic dopant because it succeed in improve the ionic conductivity of the 2HEC film.

1. Introduction

Solid biopolymer electrolytes (SBEs) is one of the most active areas of study in material research for several years. They caught the attentions of many researchers because of their excellent properties to be used in small electrical devices such as batteries. They are mechanically stable, lightweight, environment friendly and has no leakage problem when used as electrolyte. SBEs were prepared by doping the host polymer with various type of ionic dopant which, can hugely increase the electrical properties of the host polymer [1, 2]. Some application that are suitable for use of SBEs are in solid-state batteries, supercapacitors, power windows and many other solid-state electrochemical devices [3-5]. SBEs usually consist of a crystalline phase-that possess a regular structure with immobile ions, and an amorphous phase having no regular structure with mobile ions [6-10]. A few research groups have demonstrated this phenomenon and revealed the biphasic structure of SBEs [11, 12].

The arrangement of the polymer molecules greatly affects the physical properties, chemical behaviour and reactivity of the SBEs. In solid state, the movement of ions mostly occurred in the amorphous phase and moving from one site to another by hopping mechanism [13-15]. Proton conducting polymer is a special class of solid electrolytes with hydrogen ions acting as charged carriers,

which was first suggested by Rogers and Ubbelohde, in 1950 [16] and many more researchers subsequently [17-19]. The hopping of ions lead to the increase in ionic conductivity of the material. This suggests that there is a close interplay of the structural nature and conductivity in ionic conducting polymer [20-22].

In this work, a new type of SBEs based on 2-hydroxyethyl cellulose (2HEC) doped with glycolic acid were prepared. 2HEC is one of the cellulose derivatives created by means of etherification. This polymer is widely used in cosmetic, latex paints, building materials, cleaning product and even used as an oilfield chemical as a lubricant, along with many other specialty applications [23-25]. Pharmaceuticals also used 2HEC combined with hydrophobic drugs in capsule formation to improve dissolution [26]. 2HEC is a water-soluble polymer that acts as thickener, binder, emulsifier, stabilizer, film former, and exhibits pseudo-plastic solution behaviour, tolerates salts and retains water. As a good sorbent, 2HEC has a good affinity of ions due to the presence of many polar hydroxyl functional groups that can serve as coordination sites for permanent or temporary ion attachment [27-32]. The ionic conductivity of a polymer can be enhanced by introducing a good ionic dopant into the polymer system, which promotes the dissociation of proton (H^+).

GA is a weak acid base that is a naturally occurring material and it is environmentally friendly. Although many reported that ammonium salt is a good ionic dopant, it is interesting to investigate the GA behaviour as an ionic dopant. This is because GA can undergo partial dissociation, which produces proton (H^+) as a dissociated charge together with glycolate anion ($RCOO^-$), and the charged monomer attached to the backbone of GA [33-35] that eventually can enhance the ionic conductivity of the polymer host. In addition, it is also environmentally friendly. Hence, GA was chosen as an ionic dopant to 2HEC for this work. The 2HEC, GA and 2HEC-GA SBEs were characterised using EIS, FT-IR and XRD to investigate its ionic conductivity and structural properties. To the best of our knowledge, there are no published works on the 2HEC-GA SBEs; therefore, it is a great opportunity to investigate the effect of GA on the properties of 2HEC biopolymer.

2. Materials and Methods

Materials. The materials used to prepare the SBEs are 2-hydroxyethyl cellulose (2-HEC) from Sigma Aldrich, Glycolic acid (GA) from Merck and distilled water as solvent. Firstly, dissolved 2HEC in distilled water, then doped with a GA from 10 wt.% to 50 wt.% at 10 wt.% increments. Stir the solution until homogenous and by using solution casting technique, the solution were dried in oven at 60°C. Completely dried samples were stored in desiccators to prevent moisture contamination. Table 1 lists the sample designation in this work.

Table 1. Sample designation

Sample	Carboxymethyl cellulose (CMC) (g)	Glycolic acid (GA) (wt.%)
GA0		0
GA10		10
GA20		20
GA30	2	30
GA40		40
GA50		50

Experimental techniques. The SBEs were characterised using Electrochemical Impedance Spectroscopy (EIS), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffractometer (XRD). The ionic conductivity of the SBEs were measured using HIOKI 3532-50 LCR Hi-Tester interfaced

with a computer in the frequency range from 50 Hz to 1 MHz. The measurement setup was as depicted in Figure 1. The ionic conductivity of the SBEs was calculated using Equation (1).
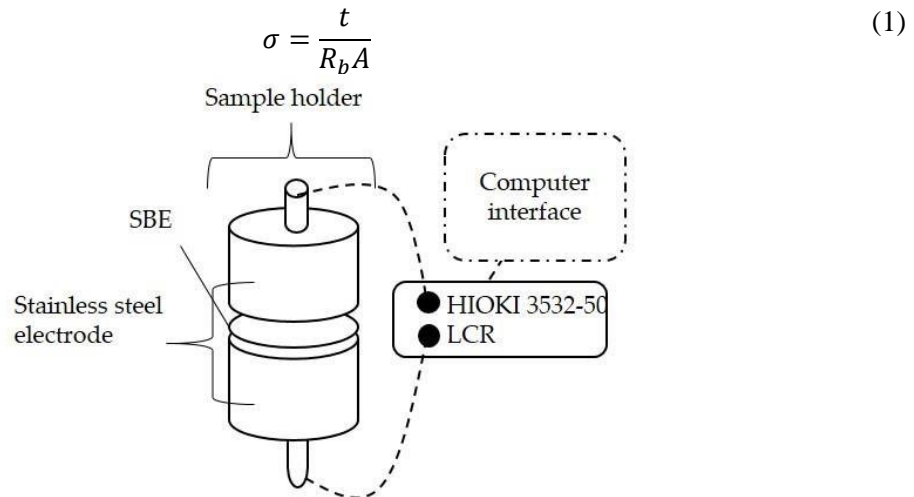
$$\sigma = \frac{t}{R_b A} \tag{1}$$

Figure 1. EIS measurement setup.

In the equation, σ is the ionic conductivity, t is the thickness of SBE (cm), R_b is a bulk resistance (Ω), and A is the contact area of the SBE and electrode (cm^2) [2, 11]. A Thermal Nicolet 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory was used to analyse the structure of the SBEs. They were scanned at frequency that ranged from 4000 cm^{-1} to 700 cm^{-1} with a resolution of 4 cm^{-1} at ambient temperature. The percentage of free ions were determined from FT-IR deconvolution that were utilised using Origin 8 fitting software based on the Gaussian-Lorentz function [21]. The free ions (%) can be calculated by using Equation (2)

$$percentage\ of\ free\ ions\ (\%) = \frac{A_f}{A_f + A_c} \times 100\% \tag{2}$$

XRD analysis was done by using a Ringaku MiniFlex II Diffractometer. Before the procedure, 2HEC-GA SBEs were cut into suitable size, then adhered onto a glass slide before being placed in the sample holder of the diffractometer. The SBEs were directly scanned at Bragg's angles of 2θ, between 5° and 70° with CuKα source radiation (wavelength =1.5406 Å).

3. Results and Discussion
3.1 Ionic Conductivity Analysis
Figure 2a shows the Cole-Cole plots for selected samples GA0 and GA40 (inset). Cole-Cole plot for GA0 has semicircle and spike region where they can be related to the SBE being partially resistive and capacitive. Cole-Cole plot for GA40 shows no semicircle and it can be a sign of increased ionic mobility (Ahmad & Isa, 2015). Bulk resistance R_b, value can be determined from the interception of the semicircle and inclined spike with the Z_r-Axis. Figure 2a shows the examples on the determination of R_b value from Cole-Cole plot for sample GA0 and GA40 respectively.

The ionic conductivity of the SBEs was plotted in a graph of ionic conductivity against the GA wt. % and depicted in Figure 2b. From the graph, the ionic conductivity of 2HEC SBE increased with the addition of GA concentration. Pure 2HEC SBE has ionic conductivity of 3.43 x 10^{-6} S cm^{-1} and with the addition of 40 % GA, the ionic conductivity increased to 4.01 x 10^{-4} S cm^{-1}, which is almost two degrees more. Early observation shows that GA is a good ionic dopant to 2HEC. The increased ionic conductivity can be related to the increased number of free mobile ions in the polymer system, thus increasing the number of ionic conduction, which is a significant factor in enhancing the ionic conductivity of the SBEs [44, 46].
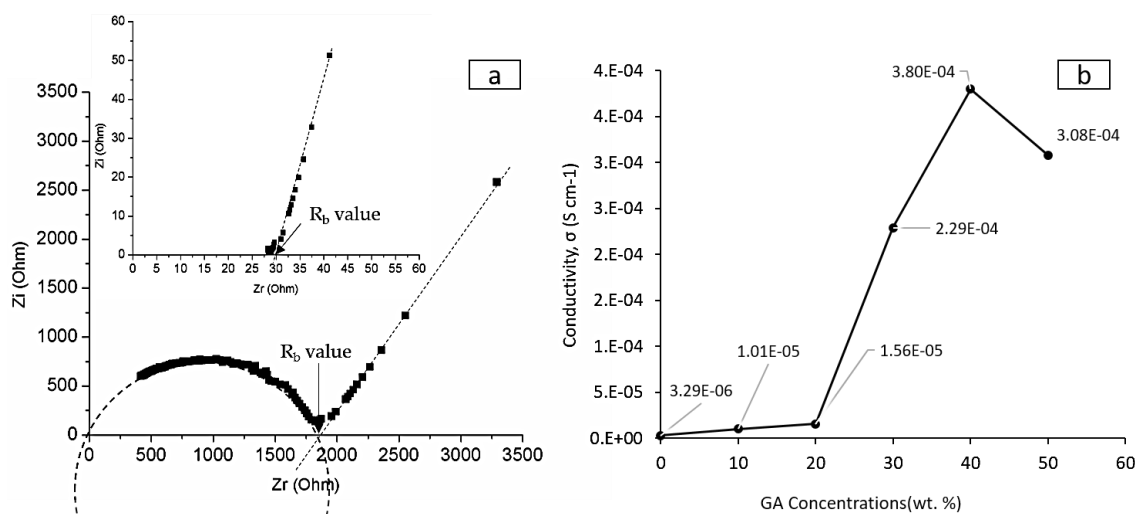
Figure 2. Cole-Cole plot; (a) GA0 and GA40 (inset), and (b) Ionic conductivity versus GA concentrations plot.

3.2 FTIR Analysis of Simple Organic Acid

The FTIR spectra of GA, 2HEC and 2HEC-GA in a range of 1200-1800 cm^{-1} were shown in Figure 3. From the figure, it can be seen that the addition of GA concentrations yielded two main absorption features in the 2HEC that are associated with carboxyl group. According to Hay *et al*. (2007) [36], protonated carboxylic acid (RCOOH) resulted in absorption band that correspond to the carbonyl stretch of υC=O (1690 cm^{-1} - 1750 cm^{-1}) and hydroxyl vibration, υC-OH (1200 cm^{-1} - 1300 cm^{-1}) which comprised of C-O and C-OH group. This vibration often resulted in a single and broad absorption band. According to Cabaniss and McVey, (1995) [37], these changes can be dependent on a few factors, two of which include; i) Electron density of carboxyl that was affected by the presence of electron donating or withdrawing functional group; and ii) Inter/intra-molecular hydrogen bonding involving a carboxylic oxygen or a proton. These two factors are typically affected more consistently and predictably in the υ_{as} mode relative to the others, making it a useful indicator of structural complexation. However, in this work, the appearance of a υ_{as} peak cannot be observed due to the overlapping of naturally absorbed water band of 2HEC (~1647 cm^{-1}) and the changes are most consistently observed at the υ_{s} mode of carboxyl group [46].
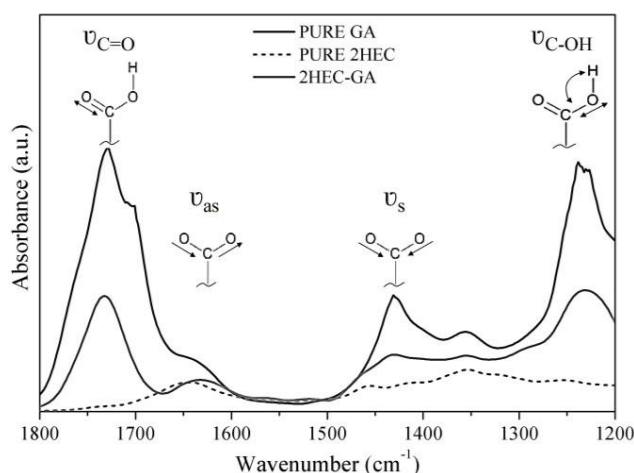

Figure 3. FTIR spectra of pure GA, pure 2HEC and 2HEC-GA (40%) film at the 1200-1800 cm^{-1} spectra region.

3.3. FTIR Analysis of 2HEC-GA SBEs

The complexation of GA and 2HEC was observed in FTIR analysis. Figure 4 represents the FTIR spectrum of pure 2HEC and 2HEC-GA system separated by four region (a) 1150-1350 cm^{-1}, (b) 15001800 cm^{-1}, (c) 900-1200 cm^{-1} and (d) 1400-1500 cm^{-1}, respectively. From the figure, the peak intensity for both υC-OH and υC=O of GA in the spectrum of 2HEC-GA system experienced a reduction in intensity, which due to the deprotonation state of GA (dissociation of H$^+$) in the SBE system. The absorption bands localized at ~1237 cm^{-1} and ~1730 cm^{-1} were due to the stretching vibrations of single and double CO bonds of the carboxylate group of GA, respectively. They are the characteristic features of the IR spectrum of GA and the increased intensity with higher GA concentration is expected. In Region c, the peak at ~1055 cm^{-1} is attributed to the υC-O of 2HEC. With the addition of GA, the band shifted to a higher wavenumber to ~ 1086 cm^{-1}. This confirms the complexation of both the host polymer and ionic dopant.

From Region (d), it can be observed that a new peak emerged at ~1440 cm^{-1} for sample GA10, which is believed due to the interactions between 2HEC and GA. The band corresponds to symmetric υ_sCOO, which was affected by the increment of GA concentration. With the addition of GA, the band shifted to a lower wavenumber to ~1436 cm^{-1} and the intensity of the peak increased. These significant changes can be associated with the formation of anionic and cationic species through higher dissociation of ionic dopant, thus allowing protonation on 2HEC chain structures. The 2HEC and GA peaks observed in this work are comparable with other works where all the peaks were found at their own specific range [2434].
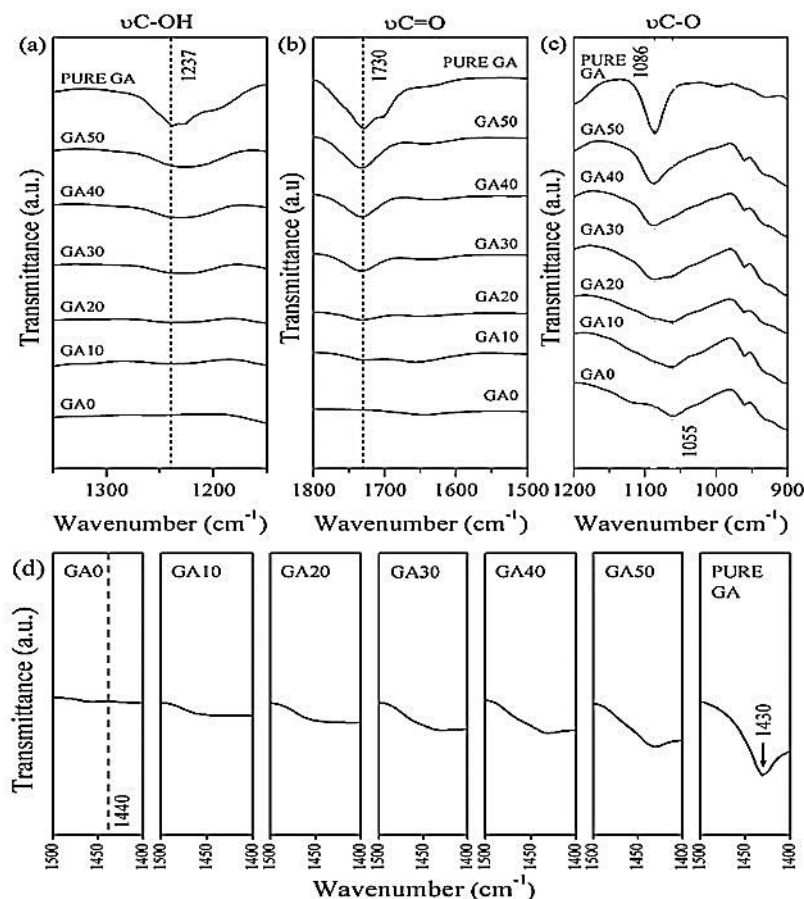

Figure 4. FTIR spectrum of 2HEC-GA system in the (a) 1150-1350 cm^{-1}, (b) 1500-1800 cm^{-1}, (c) 9001200 cm^{-1} and (d) 1400-1500 cm^{-1} region.

3.4 FTIR Deconvolution

FTIR deconvolution was performed to isolate the possible peaks presence, intensity change and shifting of the bands, hence further determine the contribution of H^+ ions as a charge carrier in 2HEC-GA SBE system [21, 22, 38]. The deconvolution was based on the Gaussion-Lorentz function and was done using Origin 8 fitting software. The sum of the intensity of all the deconvoluted peaks was ensured to fit the original spectrum where regression value of each peak is approximately unity (R^2 = 0.9998). The deconvolution peaks of $\upsilon_s COO^-$ were depicted in Figure 5.
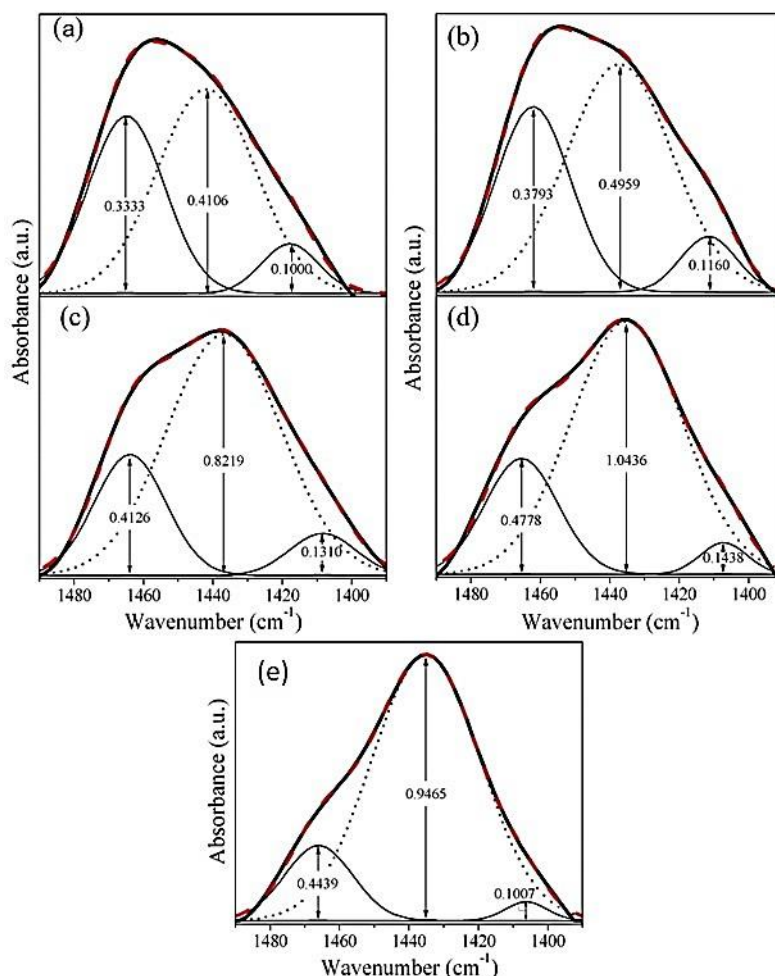

Figure 5. FTIR deconvolution of 2HEC: (a) 10%, (b) 20%, (c) 30%, (d) 40%, (e) 50% of GA in 1390-1490 cm^{-1} spectra region.

The band representing the free ions can be found in region between ~1390 cm^{-1} and ~1490 cm^{-1} where the symmetric vibration of carboxylate anion ($\upsilon_s COO^-$) is at, this is comparable to work done by Hay & Myneni (2007) [36]. From Figure 4, the peak located at ~1407 cm^{-1} can be assigned to contact the ions peak, meanwhile the peak at ~1465 cm^{-1} is the C-H characteristic band of 2HEC. It can be observed that peak intensity of glycolate anion increased with increasing GA concentration with maximum concentration at 40 wt. % and then slightly decreased at 50 wt. %. This increment could indicates the increase of number of mobile ions and this was shown in Figure 6 where the percentage of free ions alongside with ionic conductivity in a function of GA concentrations were plotted. Here, it is observed that the percentage of free ions increased until GA40 and then decreased at GA50, which in agreement with the hypothesis mentioned earlier.

With the addition of GA concentrations, more free ions dissociated into the polymer system, promotes ionic conduction and then enhanced the ionic conductivity of the SBE. Whereas at GA50, the percentage decreased and it can be attributed to the free ions start to associates back creating clusters of ions. This led to decreased in ionic conductivity of the SBE. From the observation, it can be simplified that the high ionic conductivity of GA40 was due to the high number of free ions. High contact ion percentage can be related to the ions that did not dissociate, hence explaining the low ionic conductivity of the SBE [45].
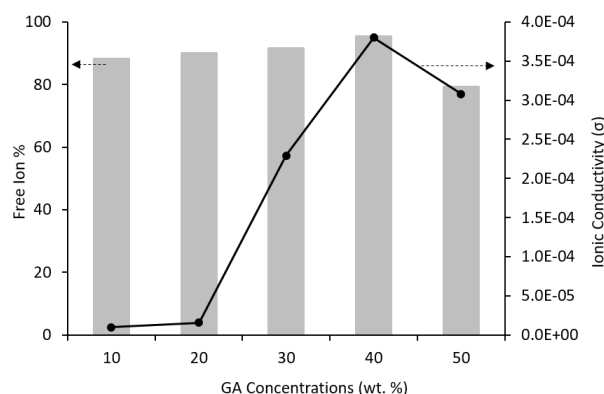

Figure 6. Percentage of free ions and ionic conductivity in a function of GA content.

3.5 XRD Analysis

2HEC is a cellulosic material that consists of crystalline and amorphous domains in various proportions [39, 43]. The reactivity and chemical behaviour are strongly influenced by its structural nature where most of the reactant penetrates only the amorphous regions. It has been reported that cellulose has the most intense reflection peak centred approximately at $2\theta \sim 22.00°$. Figure 7 shows the X-ray pattern for all SBEs and pure GA. Here, it is observed that the pure GA has multiple crystalline peaks that reveal the crystalline nature of the material. Meanwhile, there are no distinctive crystalline peaks observed in the SBEs, which indicated that GA has completely solvate in the polymer system. In a work done by Attia and Elkader (2013), they reported that the peak attributed to crystalline domain of 2HEC was situated at $2\theta = \sim22.00°$. In this work, pure 2HEC film shows intense reflection peak at $\sim21.28°$, which represent the strongest cellulose peak of the crystalline domain in the polymer host [24]. The broadened cellulose peak with the incorporation of GA concentrations indicates the SBEs are in amorphous state.
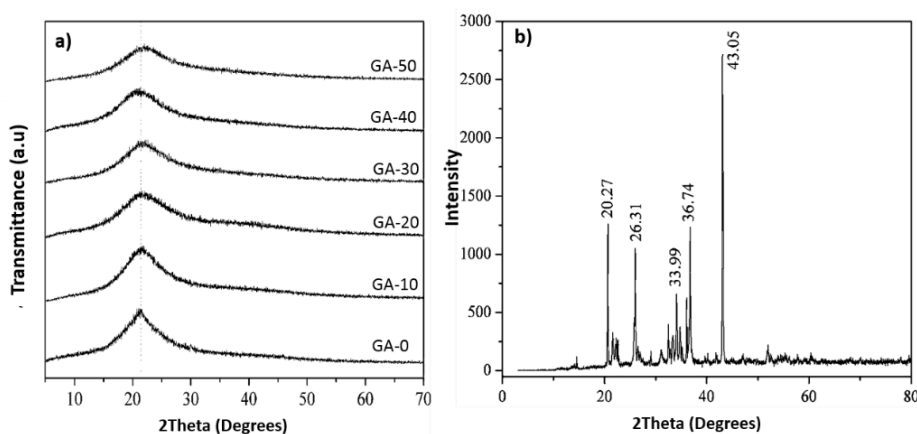

Figure 7. X-ray diffractograms (a) all SBEs, (b) pure GA.

4. Conclusions

Solid biopolymer electrolytes based on 2HEC doped with various GA concentrations was successfully made via solution casting technique. The highest ionic conductivity achieved was 3.80 x 10^{-4} Scm^{-1} for a sample with 40 wt.% GA concentration at room temperature. FTIR revealed the interactions between the host polymer and ionic dopant was from the shifted peaks of υC-O and υC-OH vibration mode. The highest conductive sample possess the highest number percentage of free ions hence confirms the relations that a high number of free ions helps in increasing the ionic conductivity. X-ray diffraction analysis shows all the SBEs are in an amorphous state with no crystalline peak detected. It can be concluded that GA is an effective ionic dopant because it successfully increased the ionic conductivity of the 2HEC.

5. References

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