Conduction mechanism via correlated barrier hopping in EC-plasticized 2-hydroxyehyl cellulose-ammonium nitrate solid polymer electrolyte

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Abstract. This present work discussed the ionic conductivity and ionic conduction mechanism of solid polymer electrolyte (SPE). The SPE was prepared from 2-hydroxyethyl cellulose incorporated with ammonium nitrate and plasticized with ethylene carbonate (2-HEC-AN-EC) via well-known solution casting method. All SPEs were characterized using electrical impedance spectroscopy (EIS). It was found that the ionic conductivity at elevated temperature obeys Arrhenius rule. The plot of frequency exponent s against temperature shows that the correlated barrier hopping (CBH) was the best model to explain the ion conduction through 2-HEC-AN-EC SPE.

Keywords: 2-hydroxyethyl cellulose, ethylene carbonate, solid polymer electrolyte, correlated barrier hopping model.

1. Introduction

Solid polymer electrolytes (SPE) are of growing important in the field of materials science. An ideal SPE must have high ionic conductivity so that it can be utilized as a conducting medium in solid-state proton battery. A good approach for ionic conductivity improvement is by understanding the ionic conduction mechanism in SPE. The variation of ionic conductivity can be divided into two parts, the frequency dependent and frequency independent component.

As proposed by Jonscher in 1977, variation of ionic conductivity in frequency dependent region can be analyzed based on Universal Power Law (UPL) or so-called Universal Dielectric Responses [1]. There are four well-known theoretical hopping models have been proposed; i) quantum mechanical tunneling (QMT) [1-4], ii) small polaron hopping (SPH) [5,6], iii) correlated barrier hopping (CBH) [7-10] and overlapping large polaron tunneling (OLPT) model [10].

Previous paper has reported the ionic conductivity of 2-HEC–AN–EC SPE at room temperature, where the highest ionic conductivity of $(1.17\pm0.01) \times 10^{-3}$ Scm^{-1} was obtained after plasticized with 16 wt.% EC [11]. Hence, the aim of this study is to determine the best conduction model for that system. Electrical impedance spectroscopy (EIS) was used to study the ionic conductivity on the effect of frequency. The result obtained from this study was then used to correlate the conduction mechanism and ionic conductivity enhancement of the SPE.

2. Experimental method

2.1. Preparation of solid polymer electrolyte

2-HEC–AN solution was prepared follows the work done by Hafiza and Isa, 2017b. Various amount of ethylene carbonate (EC) were then added into the solution and continuously stirred until complete dissolution. The homogenous solution was poured into glass petri dishes and left in oven at 50 ºC for drying process. The dried SPEs were then kept in desiccator to remove any residual moisture. The designation and composition of 2-HEC–AN–EC SPE was shown in **Table 1**.

Table 1. Designation and composition of 2-HEC–AN–EC SPE.

Designation of SPE	Composition				
	2-HEC (g)	AN (wt.%)	AN (g)	EC (wt.%)	EC (g)
P1	2.0	12	0.273	0	0.000
P2				4	0.095
P3				8	0.198
P4				12	0.310
P5				16	0.433
P6				20	0.568
P7				24	0.718
P8				28	0.884

2.2. Characterization of solid polymer electrolyte

2-HEC–AN–EC SPE was characterized using electrical impedance spectroscopy (EIS) model HIOKI 3532-50 LCR Hi-Tester. Prior to characterize, the SPE film was cut into 2 cm diameter and placed between two stainless steel blocking electrodes of the sample holder. The SPEs were tested in various frequency range (50 Hz to 1 MHz) at elevated temperature (303 K to 373 K).

3. Results and discussion

Figure 1 shows the plot of ionic conductivity at elevated temperature (303 K-373 K). As expected, the ionic conductivity measurement increases linearly with increasing temperature, confirming the Arrhenius type SPE where the regression value obtained is close to unity (refers **Table 2**). The increased of ionic conductivity at higher temperature may be attributed by the increase in free volume and polymer segmental motion [12,13]. When the SPE is exposed to higher temperature, the polymer chain segment receives sufficient energy to vibrate and create a bigger free volume around the polymer [14]. This, in turn increases migration of mobile proton through the polymer matrix. In Arrhenius type film, the nature of proton (H^+) transport at elevated temperature is almost similar to that occurring in ionic crystal, where ion is able to hop into neighbouring vacant site, hence increased the ionic conductivity [15]. The Arrhenius equation is expressed as Equation 1 [1, 16].

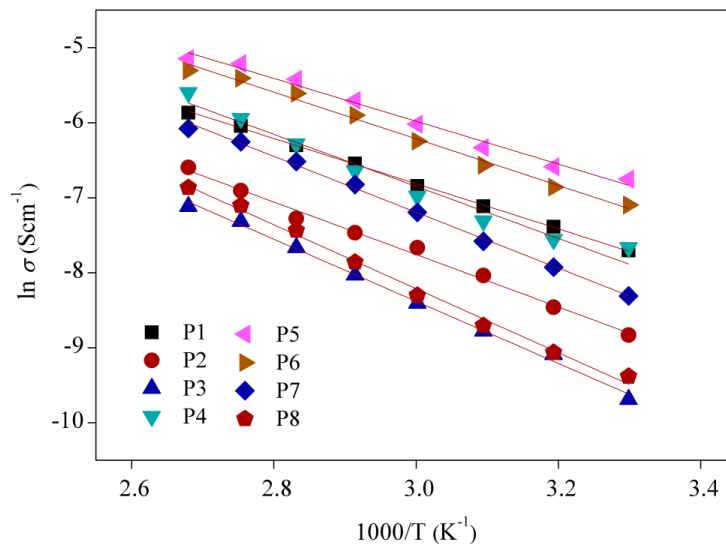$$\sigma = \sigma_o \, exp \left({-E_a}/{kT} \right) \tag{1}$$

Figure 1. Ionic conductivity of 2-HEC–AN–EC SPE at elevated temperature.

Table 2 lists the regression value and activation energy for all SPEs. The activation energy, E_a can be determined from the Arrhenius plot of ln σ against 1000/T. According to Sohaimy and Isa (2016), activation energy relates to the energy requires by the ion to release from it bond and migrate to another coordinating site through conduction process [12]. Based on this result, the SPE that exhibits the highest ionic conductivity value has the lowest E_a value. It is believed that, at lower E_a value, the H^+ ion need less energy to detach from it bond and coordinate onto the end chain of 2-HEC. The releasing and coordinating process of ion will enhance the conduction activity inside the SPE, which later increased the ionic conductivity in plasticized system.

Table 2. The regression value, R^2 and activation energy, E_a of 2-HEC–AN–EC SPE.

Sample	R^2	E_a (eV)
System 2		
P1	0.99	0.26
P2	0.99	0.35
P3	0.99	0.36
P4	0.97	0.30
P5	0.98	0.25
P6	0.99	0.27
P7	0.99	0.32
P8	0.99	0.37

Figure 2 depicts the plot of ln ε_i against ln ω for the highest conductivity SPE at elevated temperature. The study of conduction mechanism is important in SPE to describe the ion hopping between the coordinating sites. The ionic conduction mechanism was analyzed based on the Jonscher's Universal power law relationship at the higher frequency region where the effect of space charge polarization is assumed less or can be negligible [7, 9]. In this study, the acceptable frequency range is between $13 \leq$ ln $\omega \leq 16$. The power law relation is described as Equation 2 [1], as follow:

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac} \tag{2}$$

where,

$$\sigma_{ac} = A\omega^s = \varepsilon_o \varepsilon_i \omega \tag{3}$$

Consolidating and applying logarithm rule to Equation (3) gives,

$$\ln \varepsilon_i = \ln \frac{A}{\varepsilon_o} + (s-1)\ln \omega \tag{4}$$

From Equation 2 to 4, $\sigma(\omega)$ is the total of dc conductivity, σ_{dc} and ac conductivity, σ_{ac}, A is a parameter dependent on temperature, ω is equal to $2\pi f$ and s is the power law exponent in the range of $0 < s < 1$. The value of s can be calculated from the slope, m of $\ln \varepsilon_i$ against $\ln \omega$, where $m = s\text{-}1$.
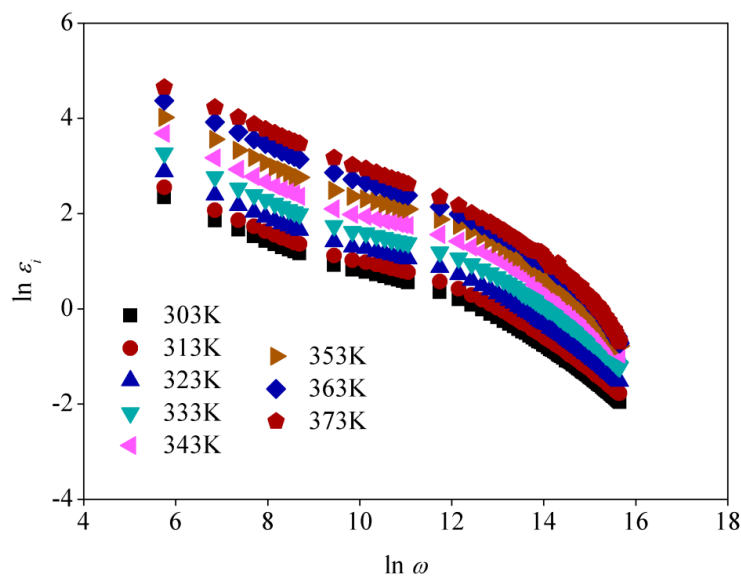

Figure 2. Plot of $\ln \varepsilon_i$ against $\ln \omega$ for 2-HEC–AN–EC SPE with the highest ionic conductivity.

Figure 3 shows the exponent s against temperature. The value of exponent s was obtained from the slope of $\ln \varepsilon_i$ against $\ln \omega$ discussed before, also was used to determine the possible conduction model for the SPE system. From **Figure 3**, it is observed that the value of exponent s decreases with increasing temperature. The appropriate conduction model can be interpreted using correlated barrier hopping (CBH) model at which the fitted equation of $s = -0.00302T + 1.28294$ gave a negative gradient in the plot. The temperature dependent of the frequency exponent s also found to obey the relation stated in Equation 5, where s is unity when T is approaching 0K [17].

$$s = 1 - \frac{6k_b T}{[W_m + (k_b T \ln(\omega \tau_o)]} \tag{5}$$

The conduction model can be further verified by comparing the value of E_a and maximum barrier height, W_m. This method was done following exactly with the work reported by Aziz et al., (2017). The value of W_m can be retrieved from the plot of $6k_b T$ against $(1\text{-}s)$ (inset plot of **Figure 3**). The W_m value obtained is 0.13 eV which is lower than E_a value (0.25 eV). This result indicates that the ions travel by way of CBH model due to the smaller barrier that exist between the two complexation sites. In this model, the H^+ ions are believed to have sufficient energy to hop across the barrier and coordinate onto another site. The presence of EC plasticizer provides a new shorter pathway between the 2-HEC and

AN which would make the ion easier to hop and require a lower E_a value. Therefore, it enhances the coordination of ion at the end chain of 2-HEC and subsequently increased the ionic conductivity.
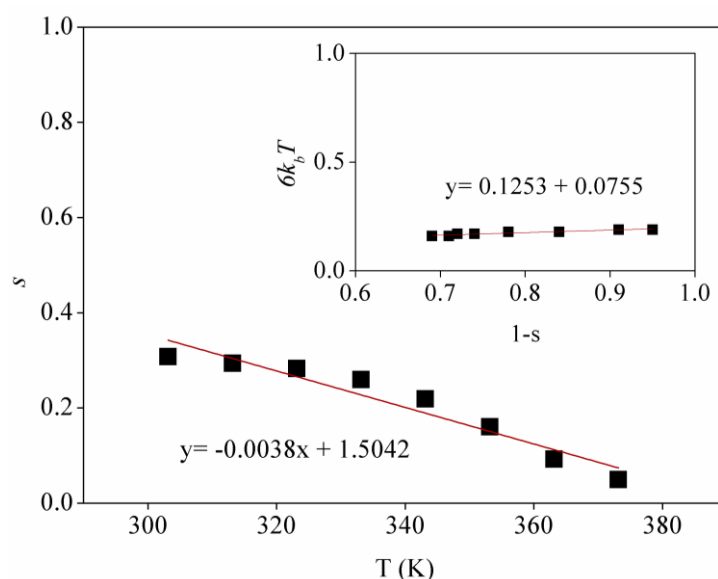

Figure 3. Plot of power law exponent s against *T* for 2-HEC–AN–EC SPE with the highest ionic conductivity. The inset represent the plot of 6kbT against (1-s).

4. Conclusion

Solid polymer electrolytes from 2-hydroxyethyl cellulose doped with ammonium nitrate and plasticized with different ethylene carbonate compositions were successfully prepared using solution casting method. The temperature dependence of ionic conductivity plot proved that all SPEs are Arrhenius type film. The SPE with the highest ionic conductivity (P5) exhibits the lowest activation energy value of 0.25 eV. From dielectric loss-frequency plot, the exponent power law, *s* was obtained. The plot of frequency exponent *s* against temperature indicated that the ionic conduction mechanism of the highest conducting SPE follows correlated barrier hopping (CBH) model.

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