



# Effect of $C_3H_4O_3$ on Band Gap Narrowing of Proton Conductive Hybrid Polymer Electrolyte

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In the present work, hybrid polymer electrolyte based on carboxymethyl cellulose-polyvinyl alcohol-ammonium nitrate-ethylene carbonate (CMC-PVA-NH<sub>4</sub>NO<sub>3</sub>-C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>) become the promising materials that has demonstrated outstanding physical properties as an electrolytes system in solar cell. In the frame of solar cell progress, the electrical conductivity and optical bandgap of polymer electrolytes are equally explored. The characterization is carried out via electrical impedance spectroscopy (EIS) and ultraviolet visible-near infrared (UV-VIS-NIR) spectroscopy. An equivalent circuit of parallel combination, bulk resistance ( $R_b$ ), and constant phase element (CPE) is obtained from transparent conductive film, CMC-PVA-NH<sub>4</sub>NO<sub>3</sub>-C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>. The optimum ionic conductivity is accomplished at  $3.92 \times 10^{-3} \text{ S cm}^{-1}$  for sample containing with 6 wt.% of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>. The absorption spectra are evaluated in the wavelength ranging from 200 to 1100 nm. Theoretical analysis reveals that the addition of 6 wt. % EC is initiating the band gap narrowing from 4.96 to 4.88 eV. The results show that the present developed materials-based polymer electrolytes have great potential for solar energy devices.

have the following considerations: 1) high ionic conductivity at ambient operating temperature ( $\sim 10^{-4} \text{ S cm}^{-1}$ ), good mechanical strength to serve as self-supported cell, 4) thermal and electrochemical stabilities, 5) excellent compatibility of electrode-electrolyte, and 6) non-hygroscopic and environmentally benign. On top of that, the optical absorption behavior of the PEs must be considered comprehensively in order to provide information about the energy band structure based on the optical transition in polymer complexes as it is important in the modification of the PEs microstructure properties.<sup>[1]</sup>

Particularly, safety issues become the main concern due to the application of synthetic and non-biodegradable polymer materials. Over the past century, there has been a vivid increase in the application of natural and biodegradable resources, signifying an astonishing evolution in the advancement of a sustainable future. Natural polymers are also known as biopolymers,

which can be classified into polyesters, polyamides, and also polysaccharides.<sup>[2]</sup> As far as biopolymers are concerned, starch,<sup>[3]</sup> sawdust,<sup>[4]</sup> chitosan,<sup>[5]</sup> tamarind seed,<sup>[6]</sup> pectin,<sup>[7]</sup> carrageenan,<sup>[8]</sup> alginate,<sup>[9]</sup> and cellulose,<sup>[10]</sup> has captured attention due to their wider electrochemical stability window, abundant in nature, low cost, and biodegradable.<sup>[11]</sup> Despite all of the advantages offered by biopolymers over synthetic polymers, its low ionic conductivity due to larger band gap of the electron excitation for the releasing of charge carrier further precludes practical applications performance. Other studies also revealed that biopolymers demonstrate a lack of stability and affects the cyclability. Therefore, the application of biopolymers has embraced various techniques to enhance those properties of biopolymer electrolytes including the addition of nano-fillers,<sup>[12]</sup> plasticizers,<sup>[13]</sup> blending,<sup>[14]</sup> or copolymerization.<sup>[15]</sup>

Herein, the present work is to report the effect of incorporating C<sub>3</sub>H<sub>5</sub>O<sub>3</sub> into biopolymer electrolyte based on carboxymethyl cellulose/polyvinyl alcohol (CMC-PVA) doped ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), which represents the hybrid polymer electrolyte (HPE). As reported in our previous work,<sup>[16]</sup> hybrid polymer upon blending has been specifically highlighted based on carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), which properties has improved without chemical synthesis. Later, subsequent study on the addition of ionic dopant was also reported<sup>[17]</sup> where further enhancement in the ion conduction properties has been explored through the addition of

## 1. Introduction

The study of polymer electrolytes (PEs) is involving the fields of macromolecular science, organic and inorganic chemistry, and also electrochemistry. Understanding on various field related to optical materials based on PE is essential for a wide range of applications, including photochemical and electrochemical displays, fuel cells, high energy rechargeable batteries, and supercapacitor. The application of PEs in device application should

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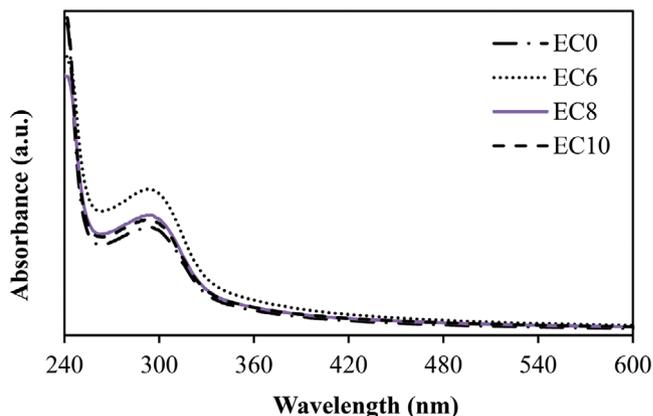
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ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Addition of  $\text{C}_3\text{H}_5\text{O}_3$  can be considered as an alternative for the imbalance enhancement in the mobility of electrons and holes owing to the electrostatic constraint of the HPE based on biopolymer materials. Light absorption by the HPE is expected to improve the charge current and narrowing the conduction band. Therefore, the HPE were characterized via UV-vis and electrical impedance spectroscopy (EIS). This present work discloses the perspective of HPE, which possessed essential properties such as (i) broad absorption band, (ii) lower band gap, (iii) reduced resistance, and (iv) higher ionic conductivity. Without a doubt, this HPE system holds great promise in the long perspective of optical device application where low-cost alternatives and green energy materials are desirable.

## 2. Result and Discussion

The optical absorbance spectra were generated from UV-visible transmittance data and presented in **Figure 1**. Based on the figure, all HPE samples demonstrated good absorbance behavior within the visible range of 240 to 600 nm. Apparently, the spectra show a peak at 300 nm, which was corresponding to the conjugated system of the carboxyl group ( $-\text{COO}^-$ ) where complexation was expected to take place within the HPE system.<sup>[18]</sup> Peak intensity was observed to increase as  $\text{C}_3\text{H}_5\text{O}_3$  content increases

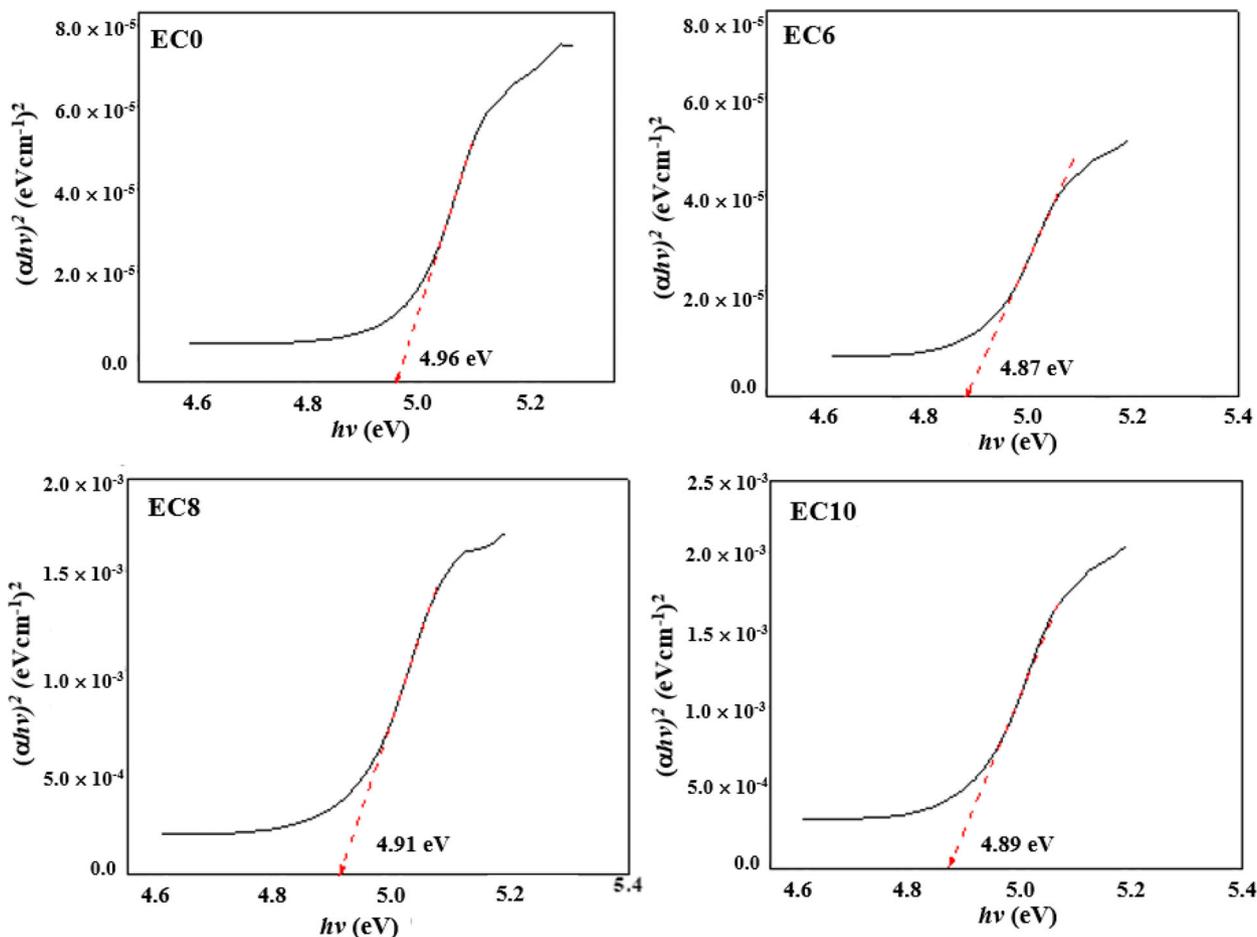


**Figure 1.** UV-Vis absorbance spectra of selected composition of the transparent conductive CMC-PVA- $\text{NH}_4\text{NO}_3$ - $\text{C}_3\text{H}_4\text{O}_3$ .

making this HPE to be captivating for the application in electrochromic devices. The optical absorption coefficient ( $\alpha$ ) was determined based on the following:

$$\alpha = \frac{2.303 A}{t} \quad (1)$$

where  $A$  is the absorbance whereas  $t$  is the thickness of the HPE.



**Figure 2.** The  $(\alpha \cdot h\nu)^2$  vs  $h\nu$  curve of selected composition of the transparent conductive CMC-PVA- $\text{NH}_4\text{NO}_3$ - $\text{C}_3\text{H}_4\text{O}_3$ .

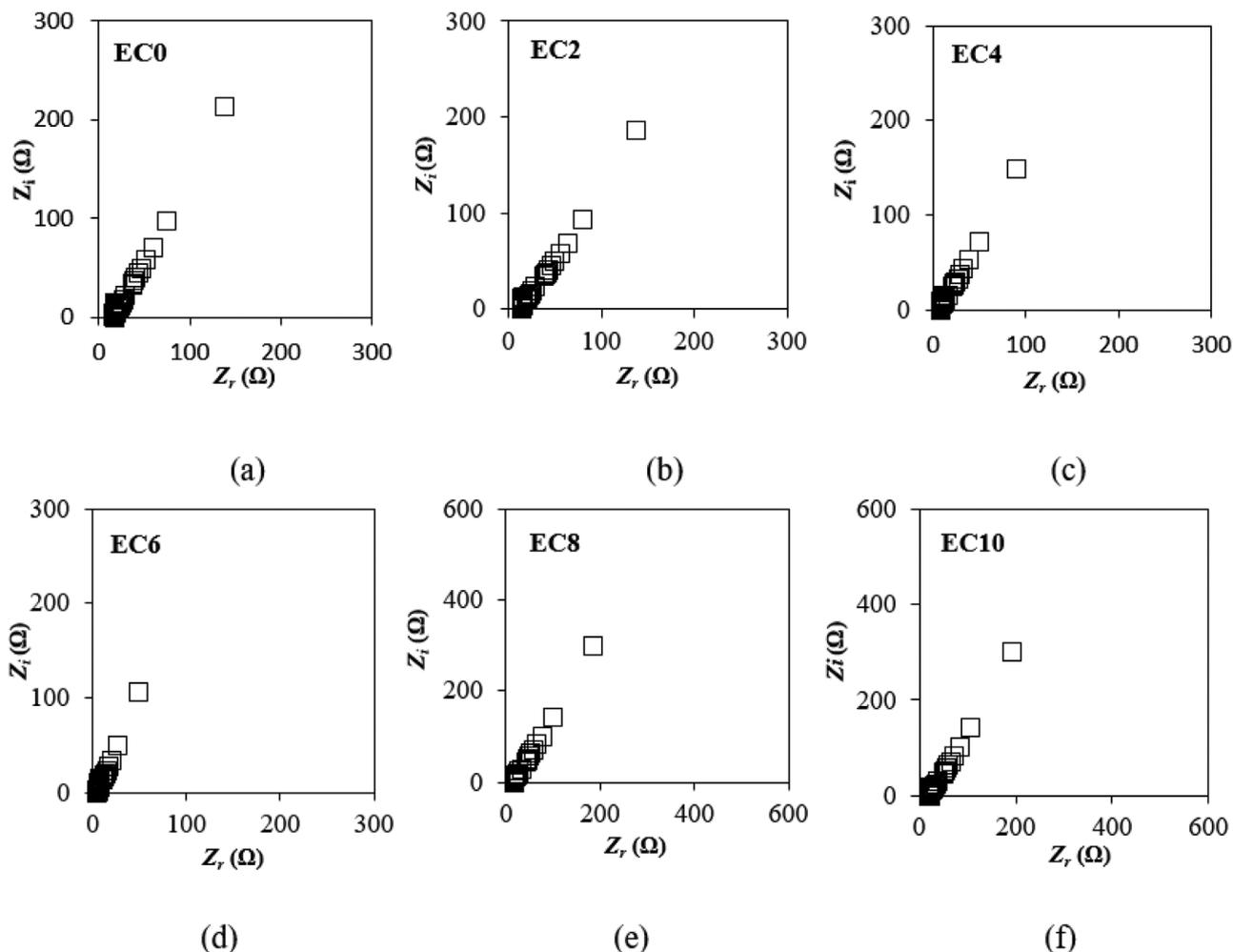


Figure 3. Cole-Cole plot of various composition of CMC-PVA-NH<sub>4</sub>NO<sub>3</sub>-C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>.

Figure 2 shows the variation of  $(\alpha \cdot h \cdot \nu)^2$  against  $h \cdot \nu$  (photon energy) owing to the existence of band gap where the absorption coefficient is related to the energy of incident photon based on the following relationship:

$$\alpha \cdot h \cdot \nu = \gamma (h \cdot \nu - E_g)^{1/2} \quad (2)$$

where  $\gamma$  is a constant,  $h$  is the Planck's constant,  $\nu$  is the frequency of light whereas  $E_g$  is optical band gap. Figure 2 shows two distinct characteristics which are linear and non-linear region. Based on Figure 2, optical band gap of the HPE was determined based on the extrapolation of the linear region to the  $x$ -axis.<sup>[19]</sup> It can be seen that the value of band gap energy ( $E_g$ ) decreases with increasing C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> with value of 4.87 eV. This  $E_g$  reduction demonstrates that the transition of electron from valence to conduction band occur more readily thus exhibiting more semiconducting nature for the present HPE system.<sup>[20]</sup> Whereas, the nonlinear region was ascribed to a defect states due to a residual absorption of the polymer complexes which become more apparent beyond addition of 6 wt. % C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>.<sup>[21]</sup> It is noteworthy that the optimum addition of

C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> into the CMC-PVA-NH<sub>4</sub>NO<sub>3</sub> could be a favorable platform for narrowing the band gap and hence improving the ionic conduction of the HPE system.

In this work, the Cole-Cole plot (Figure 3) based impedance analysis for the HPE system showing the appearance of inclined spike which can be represented by a series combination of bulk resistance ( $R_b$ ) and constant phase element (CPE). Remarkably, the addition of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> led to the disappearance of the semicircle, indicating the presence of more mobile ions.<sup>[22]</sup> Furthermore, the absence of the semicircle may be due to the ruling effect of the resistive element of the polymer.<sup>[23]</sup> The occurrence of tilted spike at the angle  $\leq 90^\circ$  was ascribed to the inhomogeneous nature of the electrode-electrolyte interface.<sup>[24]</sup> As observed in the Cole-Cole plot, the addition of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> causes the plot to move towards a higher frequency region which was attributed to faster dipolar relaxation, hence reducing the  $R_b$  value.

The determination of  $R_b$  was done based on the interception between higher and lower frequency from the Cole-Cole plot of complex impedance.<sup>[22-23]</sup> CPE was utilized in a model to replace the capacitor to balance the heterogeneity of the HPE system

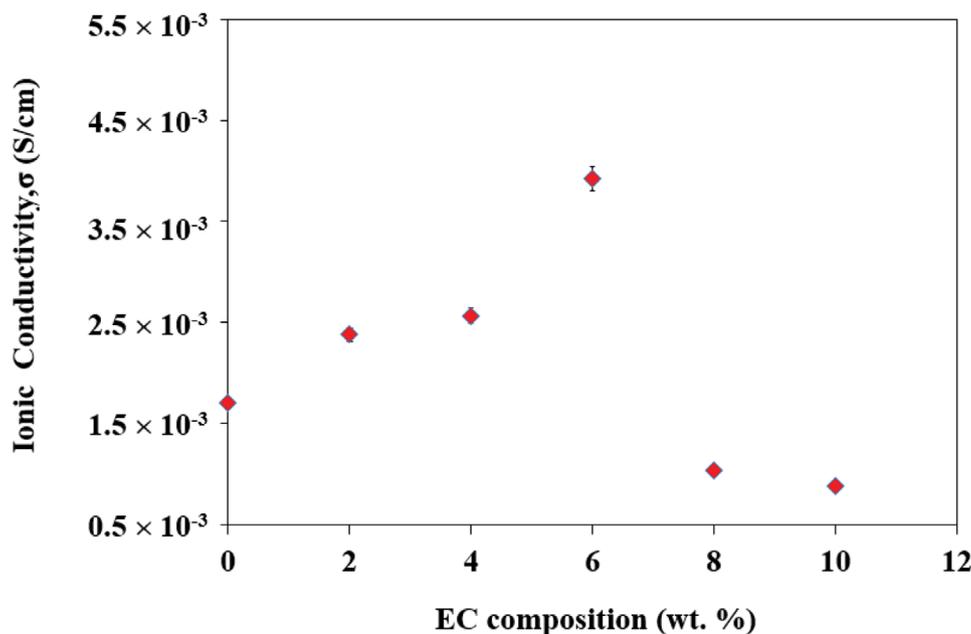


Figure 4. Ionic conductivity of CMC–PVA–NH<sub>4</sub>NO<sub>3</sub> with various composition of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>.

studied in this work. The impedance of CPE ( $Z_{CPE}$ ) can be represented by the following equation:

$$Z_{CPE} = \frac{1}{C\omega^p} \left[ \cos\left(\frac{\pi p}{2}\right) - i \sin\left(\frac{\pi p}{2}\right) \right] \quad (3)$$

where  $C$  is the capacitance of  $CPE$ ,  $\omega$  is angular frequency ( $\omega = 1/f$ ;  $f$  is the frequency in Hz), the parameter  $i$  is  $\sqrt{-1}$  and  $p$  is related to the deviation of the plot from the axis which is in radian. The values of  $Z_r$  and  $Z_i$  associated to the equivalent circuit can be expressed as:

$$Z_r = R_b + \frac{\cos\left(\frac{\pi p}{2}\right)}{C\omega^p} \quad (4)$$

$$Z_i = \frac{\sin\left(\frac{\pi p}{2}\right)}{C\omega^p} \quad (5)$$

Figure 4 shows the ionic conductivity variation upon the incorporation of different composition of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> into CMC–PVA–NH<sub>4</sub>NO<sub>3</sub>. Notably, the ionic conductivity trend was observed to increase gradually from sample EC2 to EC6 owing to the decreasing in  $R_b$  value as discussed previously and achieved its optimum value at  $3.92 \times 10^{-3} \text{ S cm}^{-1}$  for sample EC6.

The addition of plasticizer is one of the strategies that further enhanced the ionic conductivity of polymers. C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> is believed to be able to weaken the coulombic force experienced by the cation and anion, thus releasing the ion of interest (H<sup>+</sup>) more easily.<sup>[25]</sup> The ions were then led to the complexation which involved bond breakage in [H–NH<sub>3</sub>]<sup>+</sup> and allowing the oxygen to be more occupied. Thus, the oxygen become more susceptible to permit large numbers of H<sup>+</sup> to migrate without restriction. However, the ionic conductivity appeared to be decreasing beyond

sample EC8 and EC10, which may be attributed to the suppression in the dissociation of ionic dopant which led to congested of the polymer blend complexes. This would cause a considerable amount of H<sup>+</sup> unable to be captured in the CMC–PVA–NH<sub>4</sub>NO<sub>3</sub> system. Consequently, the transportation of charge carriers was reduced because of the limitation of ionic mobility.<sup>[26]</sup>

### 3. Conclusion

Hybrid polymer electrolyte (HPE) based on CMC–PVA–NH<sub>4</sub>NO<sub>3</sub> plasticized with different amount of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> (2–10wt. %) for application as a host in electrolytes system was successfully prepared. UV-vis absorption spectra revealed a decrease in optical band gap from 4.96 to 4.88 eV upon plasticized with 6 wt. % of C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> due to formation of the charge transfer complexes between the CMC–PVA–NH<sub>4</sub>NO<sub>3</sub> and C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>. The HPE was exposed to 50 Hz until 1 MHz of electric field at room temperature, 303 K. This study shows that the modification of the HPE using C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> managed to decrease the  $R_b$  value, which resulting in higher ionic conductivity value of  $3.92 \times 10^{-3} \text{ S cm}^{-1}$ . These findings indicate that the HPE incorporated with C<sub>3</sub>H<sub>4</sub>O<sub>3</sub> is considered as a potent system for the fabrication in electrochromic devices.

### 4. Experimental Section

**Materials and Methods:** The carboxymethyl cellulose (CMC) with molecular weight of 90 000 (Acros Organic Co.), whereas polyvinyl alcohol (PVA) with molecular weight of 70 000 (Merck Schuchardt) was prepared as the host polymer and further doped with NH<sub>4</sub>NO<sub>3</sub> as ionic dopant (MW 80.04; density 0.7 g cm<sup>-3</sup>; Merck KGaA) based on the procedure reported previously.<sup>[37, 38]</sup> Samples based on CMC–PVA–NH<sub>4</sub>NO<sub>3</sub>–C<sub>3</sub>H<sub>5</sub>O<sub>3</sub> were prepared with varying EC contents at 2, 4, 6, 8, and 10 (w/w %) using the

solution casting technique and represented as EC2, EC4, EC6, EC8, and EC10, respectively.

**Characterizations:** The optical absorption curves of the prepared HPE were generated in the wavelength range of 200–600 nm using Shimadzu UV-2600 spectrometer instrument. The AC conductivity studies were performed using computer-controlled HIOKI 3532–50 LCR Hi-Tester with applied frequency ranges from 50 Hz to 1 MHz. The sample was cut in circular shape of  $\pi$  diameter, sandwiched between two stainless steel electrodes. The bulk resistance ( $R_b$ ) value was obtained from the plot of imaginary impedance ( $Z_i$ ) versus real impedance ( $Z_r$ ) enable the calculation of ionic conductivity,  $\sigma$  determined using Equation (6) below:

$$\sigma = \frac{\gamma}{R_b A} \quad (6)$$

where  $\gamma$  is a thickness of the sample and  $A$  ( $\text{cm}^2$ ) the cross-sectional area of the HPE film.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

hybrid polymer electrolyte, impedance study, ionic conductivity, optical band gap

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