The Role of C-dots/(MnO$_2$)$_x$ (x = 0, 2, 4, mM) on Enhancing The Ion Transport in Poly (Ethylene Oxide) Based Solid Polymer Electrolytes: The Optical and Electrical Characteristics

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Abstract. In this work, solid polymer electrolytes (SPE) based poly (ethylene oxide) (PEO) have been prepared with carbon dots (C-dots) and C-dots/manganese oxide or C-dots/(MnO$_2$)$_x$ (x = 0, 2, 4 mM) addition. C-dots synthesized by low-temperature heating oven using cassava peels as a carbon source. Furthermore, C-dots/(MnO$_2$)$_x$ prepared with C-dots solution as media for reducing potassium permanganate (KMnO$_4$) into MnO$_2$. C-dots/(MnO$_2$)$_x$ solutions were characterized by UV-Vis and fluorescence spectroscopy. The SPE samples with C-dots/(MnO$_2$)$_x$ addition were characterized by electrical impedance spectroscopy (EIS). We provided the information that the presence of C-dots/(MnO$_2$)$_x$ has accelerated and facilitated the ionic transport in the SPE. These results reveal that C-dots/(MnO$_2$)$_x$ nanocomposite is a good candidate for SPE.

1. Introduction
Solid polymer electrolytes (SPE) are an essential component of fast-emerging electrochemical-based energy storage devices such as fuel cells, supercapacitors, and batteries due to their excellent volumetric stability [1–5]. The SPE consists of a polymer as a host membrane and an organic salt that produces faster conduction ions in the system. The role of the host polymer membrane is facilitated by ion transport through the coordination of polymer host sites, the amorphous phase, and the segmental motion of the polymer chain. Thus, the selected polymer used as the host membrane concerned must have functional groups containing electrons rich for ion dissociation [2, 6].

PEO is the most commonly used host membrane in the electrolyte polymer system. It included rich electron donors from the ether group in the polymer backbone, making it a strong candidate to coordinate with the available cations [1]. But, the weakness of PEO is the high crystalline phase that resulted in low ionic conductivity at room temperature [3]. On the other hand, some reports suggest that a decrease in the crystallinity phase increases the ionic conductivity [7, 8]. Another consideration is the type of salt that plays an important role in ionic conductivity. MnO$_2$ is an electrolyte salt-containing Mn$^{2+}$ ions used in the transport of ions.
Ordinarily, the MnO$_2$ extended to the PEO-based SPE system has a particular capacitance of 1370 F g$^{-1}$. This is a significant problem leading to weak ion transport, demonstrated with poor ionic conductivity [9]. Unnikrishnan et al. have successfully prepared MnO$_2$ using carbon dots (C-dots) solution as a medium for the reduction of KMnO$_4$ to MnO$_2$. Interestingly, C-dots have a more electron in carboxyl and carbonyl groups, which can be used to dissociate ion salt [10, 11].

To date, C-dots are a fluorescence material with a great deal of interest in especially energy storage and conversion fields. Ma et al. used C-dots that serve as nanofiller to improve ion conductivity on polymer electrolytes. The delocalized electrons dissociate the ions for fast transport [11, 12]. Roza et al. have successfully prepared powder C-dots from cassava peels by low-temperature heating and their as simple methods for used scale-up production of C-dots [13]. Therefore, we were inspired to use cassava peels as raw material for the synthesis of C-dots by adopting the method. The purpose of this research is to study ion transport at C-dots/MnO$_2$ in PEO-based SPE using electrical impedance spectroscopy (EIS). The concentration variation of C-dots/(MnO$_2$)$_x$ (x = 0, 2, 4 mM) in the C-dots solution was studied to determine its effect on ion transport in PEO-based SPE. Previously, the C-dots/(MnO$_2$)$_x$ solution was measured for its optical properties using fluorescence and UV-Vis spectroscopy.

2. Methods

2.1. Materials

PEO with linear formula of (-CH$_2$CH$_2$O-)$_n$ from Sigma Aldrich was used as a host membrane. KMnO$_4$ from Merck was used to produce MnO$_2$ as an electrolyte salt and also distilled water as a solvent.

2.1.1. Synthesis and Characterization of C-dots/(MnO$_2$)$_x$ in SPE Based PEO.

C-dots/(MnO$_2$)$_x$ (x = 0, 2, 4 mM) in SPE based PEO prepared by two steps. Firstly, C-dots powder synthesized by low-temperature heating using cassava peels as carbon source, as previous study [13]. Secondly, C-dots powder with 2% (w/v) concentrations dissolved in 50 mL distilled water and stirred at 80°C for 1 hour, C-dots solution are dividing in three parts with 10 mL volume, respectively. Then, 2 mM and 4mM (v/v) of KMnO$_4$ were added to C-dots solution and heated at 75°C for 2 hours under stirring [10]. C-dots without KMnO$_4$ addition was also made as a control. Furthermore, all samples were added to 2% PEO solution that also divided by three parts and prepared in 30 mL distilled water, then all samples stirred 1 hour under ambient temperature. Forward, the solutions were casted in 60 mm diameter petri disc and dried in 60°C for 24 hours. The prepared samples are labelled as shown on Table 1. The C-dots with and without MnO$_2$ content were characterized by UV-Vis and Fluorescence spectroscopy using Ocean Optics$^{\text{TM}}$ 2000 Spectrophotometer. Whereas SPE samples were characterized using electrical Impedance Spectroscopy by HIOKI 3522-50 LCR HiTESTER with copper electrode at 50 Hz until 1 MHz frequencies under room temperature.

| Table 1. Composition of the Prepared C-dots/(MnO$_2$)$_x$ and its Addition in SPE |
|-----------------|-----------------|-----------------|-----------------|
| C-dots/(MnO$_2$)$_x$ solution | Label | C-dots/(MnO$_2$)$_x$ in SPE based PEO | Label |
|-----------------|-----------------|-----------------|-----------------|
| 0 mM            | A0              | 0 mM            | SPE-A0          |
| 2 mM            | A1              | 2 mM            | SPE-A1          |
| 4 mM            | A2              | 4 mM            | SPE-A2          |

3. Result and Discussion

The visualization of C-dots/(MnO$_2$)$_x$ solution and SPE dependent PEO demonstrate the contrast as seen in Figure 2 and Figure 3. C-dots without MnO$_2$ have a yellow transparent solution, while C-dots/(MnO$_2$)$_x$ have shown a brown approach to the concentrated brown solution suggesting that MnO$_2$ has been formed in the solution. MnO$_2$ was synthesized via C-dot aided media to reduce MnO$_4^-$ to MnO$_2$. However, C-dots/(MnO$_2$)$_x$ also provided the impact of surface engineering on MnO$_2$ by functional groups of C-dots. Sohal et al. used ammonium citrate as a C-dot source and used it as a C-
dots/(MnO$_2$)$_x$, synthesis media [14]. On the other hand, Unnikrishnan et al. thought that C-dots could also reduce the oxygen species of MnO$_4^-$ to CO$_2$ [10]. Figure 1 show schematic of C-dots/(MnO$_2$)$_x$ formation.

![Figure 1. Schematic of C-dots/(MnO$_2$)$_x$, Formation](image)

C-dots have dominated by photoluminescence properties as material optic and electronic because reactive to light. It has the absorption ability of the photons as excitation energy to carried the electron in ground states to excited states. Furthermore, the electron will back to the ground state position simultaneously with emission process. However, there is some electron that vibrating. Therefore, the fluorescence caused electrons back to ground states is not completely [11, 15].

![Figure 2. The Visualization of C-dots/(MnO$_2$)$_x$ Solution](image)

![Figure 3. The Visualization of SPE Based PEO Containing C-dots/(MnO$_2$)$_x$](image)

**3.1. Optical Properties of C-dots/(MnO$_2$)$_x$, Solution**

C-dots have dominated by photoluminescence properties as material optic and electronic because reactive to light. It has the absorption ability of the photons as excitation energy to carried the electron in ground states to excited states. Furthermore, the electron will back to the ground state position simultaneously with emission process. However, there is some electron that vibrating. Therefore, the fluorescence caused electrons back to ground states is not completely [11, 15].

Figure 4 showed the absorption spectrum of C-dots/(MnO$_2$)$_x$. It was characterized at range 300 to 800 nm. The maximum peaks of C-dots/(MnO$_2$)$_x$ (x = 0, 2, 4 mM) showed wavelength ~450 nm, ~440 nm, and ~425 nm, respectively. As we can see, the absorption spectra shift while it contains MnO$_2$. On the other hand, high fluorescence spectrum as shown at Figure 5 showed that C-dots without containing MnO$_2$ (A0) have a higher fluorescence than others. C-dots which contained MnO$_2$ at sample A1 and A2 experience quenching phenomenon due to decrease of oxidation process or called as surface passivated. According to Wang et al. C-dots has an ability to carried out oxygen reduction reaction process, and we related it with reduction process on MnO$_2$ synthesis that utilize C-dots to binding the MnO$_4^-$ ions and finally formed MnO$_2$ following with C-dots/MnO$_2$ formation [11, 16].
3.2. Electrical Properties of SPE

EIS measurement of SPE was conducted at room temperature by sandwiching the SPE between two copper ion blocking electrodes with a voltage signal of ~20 mV. It examined the dielectric properties complex impedance, ionic conductivity, complex dielectric, complex electrical modulus, and phase angles. The complex situations involved electrochemical reactions, species transport, and interface interaction.

3.2.1. Complex Impedance Plot. This analysis is usually required to obtain bulk resistance value and interpreted the interactions between electrode-electrolyte interface while the charge transfer occurs. Here, a mathematical principle to obtain real and imaginary Z values can following equation (1) and (2) [17, 18].

\[
Z' = |Z| \cos \theta \\
Z'' = |Z| \sin \theta
\]

where \(Z'\) and \(Z''\) are the real and imaginary parts of the electrical impedance data, respectively. The impedance experimental data can be analysed by plotting the real \((Z')\) versus imaginary parts \((Z'')\) of SPE-A0, SPE-A1, and SPE-A2 which is showed at Figure 6, 7, and 8, respectively. We obtained a semi-circular pattern as experimental result all the polymer electrolyte system reveals similar feature [19–21]. It indicates the presence of electrolyte resistance and ends by vertical points which can be assumed as diffuse layer resistance, both phenomenon occur due to polarization process between electrode-electrolyte interface, the Mn\(^{2+}\) ions experience dissociation to collected on electrolyte interface caused by electric field and undergo to re-associate to diffuse through the layer [22].

According to the result on Figure (3a-3c), the bulk resistance of these SPE are decrease following by an increase of MnO\(_2\) content.

Based on material characteristics, due to the presence of the electron-rich ether group, PEO is the most interesting candidate as a polymer host, capable of making a complex with several salts, including dissociating MnO\(_2\) into Mn\(^{2+}\) ions. [2], so it will increase a busy region as we called by polarization to lowering the bulk resistance and enhance the ionic transport. Moreover, the presence of C-dots also will facilitating ionic transport refer to study which is conducted by Ma et al [11]. They were assumed that the carbonyl and carboxyl groups on C-dots have a play role to decrease the
crystalline region of PEO for amorphous region formation. So it has role for facilitating ion migration based on previous reported [7, 23, 24].

\[ \sigma_{DC} = \frac{L}{R_b A} \]  

3.2.2. DC Ionic Conductivity. The ionic conductivity is a key parameter for the application of SPE. It was measured at room temperature and calculated from the bulk resistance \( R_b \), thickness \( L \), and surface area \( A \) of the SPE which following the Equation (3).

According to the results, the linear information that we obtained is the relation between bulk resistance with ionic conductivity results. The ionic conductivity of SPE (as shown by Table 2) increases with the increasing of MnO₂ content due to the lowest bulk resistance. The enhancement of ionic conductivity attributed to the interaction of cation with electron-rich ether group and increase the free mobile ions [1].

| Sample code | \( R_b \) (Ω) | \( \sigma_{DC} \) (S/cm) |
|-------------|----------------|-------------------------|
| SPE-A0      | \( 1.76 \times 10^3 \) | \( 2.89 \times 10^{-8} \) |
3.2.3. Dielectric Permittivity Study. In order to understand polarization effects of SPE, analysis of dielectric properties is very important. Dielectric properties of this SPE is used to explain the ion transport mechanism and polymer segmental relaxation simultaneously [25]. Dielectric permittivity also consists by real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts or complex dielectric which can be obtained by calculated both following the equation (4) and (5).

$$\varepsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)}$$  \hspace{1cm} (4)

$$\varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}$$ \hspace{1cm} (5)

where $\varepsilon'$, $\varepsilon''$, $\omega$, and $C_0$ are dielectric constant, dielectric loss, angular frequency, and capacitance in vacuum. Angular frequency was given by $2\pi f$ where $f$ is frequency of applied field and capacitance in vacuum which given by $\varepsilon_0 A/L$, where $\varepsilon_0$, $A$ and $L$ is permittivity of free space, surface area and thickness of the samples, respectively [25–28]. Real part of dielectric represent an ability of material to stored electric charge, whereas imaginary part represent dissipation energy required to align dipoles [1, 29].

![Figure 9](image9.jpg)  
**Figure 9.** The Real Part of Dielectric Permittivity as a Function of Log Frequency

![Figure 10](image10.jpg)  
**Figure 10.** The Imaginary Part of Dielectric Permittivity as a Function of Log Frequency

As can be seen at Figure 9 and 10, both reveal an exponential spectrum which started by high values and turn down gradually following by the shift of frequency. Generally, the dielectric spectrum can interpret about ion transport process from the applied field depends on frequency [30] It explains by three-step phases, (i) at the lower frequency called electrode polarization in the SPEs interface, where it accumulates or resist the ionic dissociation that was supplied from the applied field. Thereafter, the ions will be associated with SPEs which is known by internal resistance. (ii) because of the swift ion activity, the dissociation process re-occurs at an intermediated frequency, and (iii) resulted in lowering dielectric values gradually until the ions dissociated again at higher frequency [1, 2]. The enhancement of dielectric constant and loss values are accompanied by an increase of MnO$_2$ content, so higher dielectric values are accompanied by a high polarization process on 4 mM MnO$_2$ content, whereas the lower is charges accumulation effect [29]. We assumed that Mn$^{2+}$ which as a
A conductive ion has been improved charge density, so it will enhance the diffusivities as well as utilize charge carrier which contained in the polymer chain and C-dots. In addition, sample without MnO$_2$ only accumulates charge carrier, therefore it has a higher bulk resistance in the SPE system.

3.2.4. Loss Tangen Analysis. Dielectric loss tangen (tan $\delta$) analysis as a function of frequency is defined as the ratio of dielectric loss and dielectric constant values in a periodical field or called as dissipation factor. This is an opportunity to obtained more information about the alteration of resistive ($\varepsilon''$) and capacitive ($\varepsilon'$) respond depended to frequency [31]. We obtained the plot shape of $\tan \delta$ in the Figure 11 with calculated by following the equation (6) [29].

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

The $\tan \delta$ values increase with increasing frequency, reaching its maximum value at particular frequency, and then decrease with further increasing frequency as we can refer from Koop’s phenomenological principle [29, 32]. The peaks which obtained correspond to the electrode polarization frequency [33]. There is found a peak shift depends to frequency while SPE contained MnO$_2$. This may be relates to an increase of charge density, then it caused the flexibility of polymer backbone is increase [29]. Moreover, the change in peak position shifts towards the higher frequency lead to a decrease in relaxation time, hence increase the ionic conductivity [34].

![Figure 11. $\tan \delta$ Depend Log Frequency](image)

Therefore, we assumed that is influenced by fast movement of segmental motion occurred in polymer chains [34]. Then, an enhancement of $\tan \delta$ peaks following by increase with MnO$_2$ concentration has been enhance the charge accumulation as can be seen from dielectric properties at Figure 4. Thereby, it will increase the capacitance in this SPE [35].

3.2.5. Electrical Modulus Analysis. Electrical modulus is important parameter which extensively used for better insight observed to study the bulk dielectric behaviour and suppression of electrode polarization in SPE system [36]. The real ($M'$) and imaginary ($M''$) parts of electrical modulus was calculated using the following equation (7) and (8).

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$
\[ M'' = \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} \]  

(8)

Where \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary parts of dielectric constant, respectively. Figure 6 shows the \( M' \) and \( M'' \) curves, where \( M' \) reflected a removal of electrode polarization contribution and charge carrier’s accumulation at the electrode-SPE interface, respectively [27].

The curves of the electrical modulus of both real and imaginary parts perform an exponential curve (as show by Figure 12 and 13). It starts with non-zero values at low frequency and enhances at higher frequency [25]. Non-zero values of \( M' \) in low frequency are attributed to the busy region due to the polarization effect and resulting a large capacitance associated with the electrodes according to non-Debye behaviour. Thereafter, a higher \( M' \) value is attributed to the relaxation processes [35].

![Figure 12](image1.png)  
**Figure 12.** The Real Parts of Electrical Modulus as a Function of Log Frequency

![Figure 13](image2.png)  
**Figure 13.** The Imaginary Parts of Electrical Modulus as a Function of Log Frequency

The different peak for each sample relates to bulk effect and conduction relaxation. SPE-A0 has a higher \( M' \) and \( M'' \) that indicates a high bulk effect following by lower ionic mobility in the electrode-SPE interface than samples with MnO\(_2\) addition. Therefore, SPE with contained MnO\(_2\) will improve ionic mobility and reduce the relaxation process.

4. Conclusion
The role of MnO\(_2\) which was synthesized by C-dots media has influenced optical properties such as fluorescence and absorbance spectra, which have revealed a quenching phenomenon. C-dots/(MnO\(_2\))\(_4\) addition to SPE demonstrated good dielectric properties and improved ion conductivity compared to MnO\(_2\). Reasonable ionic conductivities were therefore achieved by adding them to the PEO-based SPE method.

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References
[1] Arya A and Sharma A L 2018 *J. Phys.: Condens. Matter*. 30 165402.
[2] Arya A, Sadiq M, and Sharma A L 2019 *Mater. Today Proc.* 12 554.
[3] Das S and Ghosh A 2015 *AIP Adv.* 5 027125.
[4] Edman L, Doeff M M, Ferry A, Kerr J, and De Jonghe L C 2000 *J. Phys. Chem. B*. 104 3476.
[5] Abd Karim S R, Sim L H, Chan C H, Zainal N F A, and Kasim M A 2013 Adv. Mater. Res. 812 267.

[6] Chan C H and Kammer H-W 2017 Ion. 23 2327.

[7] Putro P A, Yudasari N, and Maddu A 2020 J. Phys.: Conf. Ser. 1491 012033.

[8] Saadiah M A, Zhang D, Nagao Y, Muzakir S K, and Samsudin A S 2019 J. Non-Crystalline Solids 511 201.

[9] Hou Y, Cheng Y, Hobson T, and Liu J 2010 Nano Lett. 10 2727.

[10] Unnikrishnan B, Wu C-W, Chen I-W P, Chang H-T, Lin C-H, and Huang C-C 2016 ACS Sustain. Chem. Eng. 4 3008.

[11] Ma C, Dai K, Hou H, Ji X, Chen L, Ivey D G, and Wei W 2018 Adv. Sci. 5 1700996.

[12] Wang X, Feng Y, Dong P, and Huang J 2019 Front. Chem. 7 671.

[13] Roza L, Fauzia V, Rahman M Y A, Isnaeni I, and Putro P A 2020 Opt. Mater. (Amst.) 109 110360.

[14] Sohal N, Maity B, and Basu S 2020 ACS Appl. Nano Mater. 3 5955.

[15] Putro P A, Roza L, and Isnaeni 2019 SPEKTRA: J. Fis. Apl. 4 11.

[16] Hiremath S D, Priyadarshi B, Banerjee M, and Chatterjee A 2020 J. Photochem. Photobiol. A Chem. 389 112258.

[17] Zhu M, Xie H, Guo J, Bai W, and Xu Z 2001 Sci. China Ser. D Earth Sci. 44 336.

[18] Aziz S B, Woo T J, Kadir M F Z, and Ahmed H M 2018 J. Sci. Adv. Mater. Devices 3 1.

[19] Aziz S B, Hamsan M H, Abdullah R M, and Kadir M F Z 2019 Mol. 24 2503.

[20] Baharun N N S, Mingsukang M A, Buraidah M H, Woo H J, and Arof A K 2018 Ion. 26 1365.

[21] Dave G and Kanchan D K 2018 Indian J. Pure Appl. Phys. 56 978.

[22] Mei B-A, Munteshari O, Lau J, Dun B, and Pilon L 2018 J. Phys. Chem. 122 194.

[23] Cheng Q, Cui Z, Li J, Qin S, Yan F, and Li J 2014 J. Power Source. 266 401.

[24] Cheang P L, Teo L L, and Lim T L 2010 IOP Conf. Ser. Mater. Sci. Eng. 11 012003.

[25] Aziz S B and Mamand S M 2018 Int. J. Electrochem. Sci. 13 10274.

[26] Aziz S B 2013 Iran. Polym. J. 22 877.

[27] Aziz S B, Abdullah O G, Saeed S R, and Ahmed H M 2018 Int. J. Electrochem. Sci. 13 3812.

[28] Aziz S B, Karim W O, and Ghareeb H O 2020 J. Mater. Res. Technol. 9 4692.

[29] Tripathi N, Shukla A, Thakur A K, and Marx D T 2020 Polym. Eng. Sci. 60 297.

[30] Aziz S B2016 Adv. Mater. Sci. Eng. 2016 2527013.

[31] Aziz S B, Marif R B, Brza M A, Hamsan M H, and Kadir M F Z 2019 Polym. 11 1694.

[32] Kopps C G 1951 Phys. Rev. 83 121.

[33] Verma M L and Sahu H D 2017 Ion. 23 2339.

[34] Gurulakshmi S, Madeswaran S, Karthikeyan S, and Porcheshiyan V 2019 Asian J. Chem. 31 1181.

[35] Aziz S B, Brza M S, Saed S R, Hamsan M H, and Kadir M F Z 2020 J. Mater. Res. Technol. 9 5410.

[36] Saadiah M A and Samsudin A S 2018 IOP Conf. Ser. Mater. Sci. Eng. 342 012045.