Int. J. Electrochem. Sci., 15**(2020)** 7434 – 7447, doi: 10.20964/2020.08.86

International Journal of
ELECTROCHEMICAL
SCIENCE
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Short Communcation

Electrochemical Characteristics of Phthaloyl Chitosan Based Gel Polymer Electrolyte for Dye Sensitized Solar Cell Application

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Received: 7 April 2020/ *Accepted:* 9 June 2020 / *Published:* 10 July 2020

In this project, a set of gel polymer electrolytes (GPEs) was fabricated using Phthaloyl Chitosan (PhCh) as a host polymer, ethyl carbonate (EC) like a plasticizer, potassium selenocyanate (KSeCN) as salt, and selenocyanogen as redox mediators to fabricate the dye-sensitized solar cells (DSSCs). The electrical properties of prepared GPE systems have been characterized by dielectric permittivity and electrical impedance spectroscopy (EIS). Through the impedance spectra, the ionic conductivity of the GPE systems was evaluated at room temperature. It was observed that the ionic conductivity of PhCh-based GPE was increased with the increase of salt amount, and the uppermost ionic conductivity is 4.76 x 10^{-2} S Cm^{-1} was obtained from the maximum content of KSeCN:$(SeCN)_2$ added salt. On the other hand, the increases of dielectric parameters (ε′, ε″) indicated that the rise of the dielectric polarization in GPE systems. The films were used to dye-sensitized solar cells (DSSC) to perceive the GPEs usefulness. For GPEs including KSeCN, the DSSC (η%) efficiency for the N3 dyes obtained was 2.28% with J_{sc}(6.19 mA/cm^2), V_{oc}(0.61V), as well as fill factor (0.60).

Keywords: phthaloyl chitosan, gel polymer electrolyte, dielectric constant, ionic conductivity, dye-sensitized solar cell (DSSC)

1. INTRODUCTION

The research on the progress of high-performance electrochemical devices has been deeply investigated to produce and store energy inexpensively. Among these materials contributed to the field of renewable energy, the polymer is a significant component. Therefore, from renewable sources, environmentally friendly polymer electrolytes become a favorable alternative for synthesis polymers [1]. One of the important applications of polymers is their suitability for electrolyte preparation that can be achieved by adding the ionic salt to the macromolecular polymer chain. In addition, there are many advantages of polymer electrolytes such as resistance to shock, vibration, resistance to variation of pressure and temperature, and natural seal. However, some drawbacks are high interfacial resistance with electrodes and low ambient conductivity which can be modified by different approaches such as blending and plasticizing [2]. Recently, many types of research were reported on chitosan due to consuming specific properties that have attracted a lot of researchers as it offers many potentials in biomedical, pharmaceutical, and industrial applications [3, 4]. Chitosan is obtained from N-deacetylated chitin that is the second greatest abundant natural polymer; and chitin undergoes alkaline hydrolysis treatment in chitosan fabricating. As it is in the form of chitosan, it constitutes a polymer host for electrolytes since it can dissolve ionic salts and able to give a high conductivity polymeric system because of the group of protonated amino in the backbone of the polymer [5-10]. Primarily, chitosan obtained from insect cuticles, the shell of crustacean, the cephalopods beaks for example arthropod exoskeletons, squids, and the fungi cell wall that including chitin. On the chain of chitosan, there are hydroxyl groups (OH) and amine (NH_2) groups that appropriate biopolymers for the dative bonds creation with ionic metals [11, 12]. Though, there are some restrictions in employing chitosan for electrolytes as a result of it is generally not soluble in all solvents of organics because it's just solvable in dilute acetic as well as formic acids, the water existence causes the metal parts corrosion when used devices. Therefore, to extend the solubility range of chitosan, the chitosan modification to phthaloyl chitosan (PhCh) was used by countless researchers. The adjustment is called phthaloylation where Nishimura and coworkers substituted a couple of groups of hydroxyls with a group of hydrophobic phthaloyl. Therefore, it destroys the structure of crystalline which means disrupts the hydrogen bonds and developed the chitosan solubility. Then PhCh becomes a valuable candidate as a host polymer in the polymer electrolytes, and it dissolves in common organic solvents for instance dimethylformamide (DMF), dimethyl sulfoxide (DMSO), as well as pyridine [13]. In dye-sensitized solar cells (DSSCs), electrolytes have a vital involvement in determining the efficiency, as well as solar cell stability. There are various types of electrolytes nowadays, and currently lots of researchers interested in a biopolymer-based electrolyte such as PhCh as an environmentally friendly material. Researches on conductivity already were done by using PhCh as host polymer for instance PhCh reacted with tetra propylammonium iodide (TPAI) which gave the ionic conductivity of 5.46×10^{-3} S/cm [14, 15]. Another conductivity which is 1.37×10^{-2} S/cm was obtained when PhCh reacted with potassium iodide (KI) [16]. The previous research showed that the PhCh has the ability to rising the conductivity of the electrolyte systems. Although, the polymer electrolytes conductivity essentially contributed by the compound of ions exists in it. So, to confirm the polymer electrolyte is conductive, the ionic compound is essential that causes the redox mediator existence. In the process conduction, the salt was employed to create mobile ions as well as redevelop the oxidized electrolyte, closing the circuit [17, 18]. The iodide/triiodide(I-/I_3-) is the greatest general redox couple that was desired as the greatest steady as well as effective in DSSC. Furthermore, the couple of I-/I_3-possesses an appropriate potential of redox, excellent solvability, and will not consume excessive light [19]. In this research, $SeCN^-/(SeCN)_3^-$ was preferred by reason of its exceptional characteristics. Earlier work was held by Bella et al. [20] employing $SeCN^-/(SeCN)_3^-$ in the electrolyte of polymer as well as they determined this redox mediator has good mass transfer properties containing valued mobility that mainly capable for GPE integration. The fabricated GPEs were employed to DSSC to detect the electrolyte effectiveness. The KSeCN:$(SeCN)_2$amount was varied, and the composition amount is on the basis of the below chemical equation:

$$SeCN^- + (SeCN)_2 \rightarrow (SeCN)_3^- \qquad (1)$$

The electrolytes effectiveness has been checked in DSSCs on the basis of mesoporous TiO_2 sensitized using dye of N3 like a sensitizer. The conductivity investigations, dielectric, as well as curve of J–V of the PhCh-based GPEs were explained in the subsequent sections.

2. EXPERIMENTAL

2.1 Chitosan modification to phthaloyl chitosan.

Low molecular chitosan with 1 g has been inserted into dimethylformamide (DMF) (30 ml) with phthalic anhydride (4.3 g) in a round-bottom flask. The solution has been warmed at 120 ^oC underneath gas of nitrogen (N_2) with continuous stirring for 6-7 hrs. Subsequently, the temperature has been reduced to 60^{o}C and the pipe of the gas that connects the gas of the nitrogen by the condenser and has been withdrawn then leftward night time. The mixture has been transferred to iced water and filtered for precipitate collection. The composed precipitate has been washed using ethanol in an extractor of Soxhlet with around 6 hrs. The last goods have been dried as well as vacuumed till around 4-5 hrs. at 60^{o}C in a vacuum oven.

2.2 Gel Polymer Electrolyte (GPE) Preparation.

To provide KSeCN/$(SeCN)_2$, the selenocyanogen is in the case of liquid, a stable quantity of 0.3 g of PhCh has been dissolved in DMF (0.8 g). The solution has been warmed in the range between 70 ^{o}C and 80^{o}C and stirred for 30 min till a homogenous solution has been attained. Then 0.8 g of ethylene carbonate (EC) has been inserted to the mixture and heated as well as has been stirred underneath a similar condition. Later, Potassium Selenocyanate (KSeCN) has been included in the mixture and heated in the range from 70 °C to 80 °C for 5 hrs. When the solution has the form of gelatin, the selenocyanogen has been included as well as agitated for 2 hrs. at ambient temperature until the solution gets homogeneous. The compositions of the salts employed in the GPEs are listed in Table 1.

Table 1. The composition of PhCh:DMF:EC:KSeCN/$(SeCN)_2$ systems based GPEs

Samples	PhCh/g	DMF(g)	EC (g)	KSeCN/mole	$(SeCN)_2$/mole
Se0	0.3	0.8	0.8	0.0000	0.0000
Se1	0.3	0.8	0.8	0.0003	0.0003
Se2	0.3	0.8	0.8	0.0006	0.0006
Se3	0.3	0.8	0.8	0.0009	0.0009
Se4	0.3	0.8	0.8	0.0012	0.0012

2.3 Selenocyanogen $(SeCN)_2$ Synthesis.

The selenocyanogen fabrication is on the basis of Oskam where KSeCN (5 mmol) has been inserted to acetonitrile (50mL). Then the mixture has been reacted with Br_2 (2.5 mmol) in acetonitrile (25mL) with agitating, and has been cooled to 0°C by means of bath water in dark. The suspension has been subjected filtration to eliminate the precipitation that is KBr. The mixture created following in a solution of yellow color of selenocyanogen that dark in color upon gradually including 10mmol of KSeCN in acetonitrile (25mL).

2.4 Characterization of GPEs.

The conductivity of ions and the mechanism of dielectric of the GPEs has been investigated via electrochemical impedance spectroscopy (EIS). The frequency has been arranged in the range from 50Hz to 5MHz using instrument of HIOKI. For the investigation of conductivity, the conductivity (σ) of ions value on the basis of the bulk resistance (R_b) was achieved from the Nyquist plot with the equation below [21-23]:

$$\sigma = \frac{t}{R_B \times A} \qquad (2)$$

where *t* refers the electrolyte thickness and A refers the electrolyte area. For the studies of dielectric, the dielectric constant (ε') and dielectric loss (ε") has been achieved by using the equation below [24-29]:

$$\varepsilon' = \frac{t}{\omega A \varepsilon_o}\left[\frac{Z''}{(Z')^2 + (Z'')^2}\right] \qquad (3)$$

$$\varepsilon'' = \frac{t}{\omega A \varepsilon_o}\left[\frac{Z'}{(Z')^2 + (Z'')^2}\right] \qquad (4)$$

2.5 dye-sensitized solar cell (DSSC)Fabrication

The glasses of Fluorine Tin Oxide (FTO) were employed like substrates and they have been rinsed and cleaned using ethanol as well as distilled water. The photoanode is composed of a couple of TiO_2 layers on a substrate of conducting glass. 0.5 g TiO_2 powder has been ground for 30 min with nitric acid (2mL) within a mortar, and drying of air for 30 min. After it has been sintered for 30 min at a temperature of 450^{o}C. The colloidal suspension of TiO_2 for the second layer has been fabricated through grinding an additional 0.5 g powder of TiO_2 with nitric acid (2 mL). Carbon wax with 0.1 g, and Triton X-100 with a few drops have been inserted to the mixture, as well as sintered in the furnace at a temperature of 450^{o}C for an hr. The electrode was cooled to a temperature of 60^{o}C as well as soaked into a solution of ethanolic N3 dye for 24 hrs. Afterward cooling, the fabricated GPEs were cast on the prepared TiO_2 photo-electrode and subsequently positioned with the electrodes of platinum-coated. The DSSCs photovoltaic performing has been detected via the electrometer of AUTO LAB. The fill factor (FF), and the conversion efficiency (η) were computed utilizing the following equations:

$$FF = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}} \qquad (5)$$

$$\eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{I_{SC} \times V_{OC} \times FF}{P_{in}} \times 100 \qquad (6)$$

where I_{max} refers the current density at the highest output power, V_{max} refers the voltage at the highest output power, and P_{in} denotes the light power incident.

3. RESULTS AND DISCUSSION

3.1Impedance Conductivity studies

Figure 1 illustrates the impedance spectra of Nyquist plots (Z_i versus Z_r) of PhCh-based GPEs for the (SE0-SE4) samples at room temperature. The effect of KSeCN salt onto ionic conductivity of the PhCh-based GPEs is well correlated by adding varying content of KSeCN salt at room temperature.

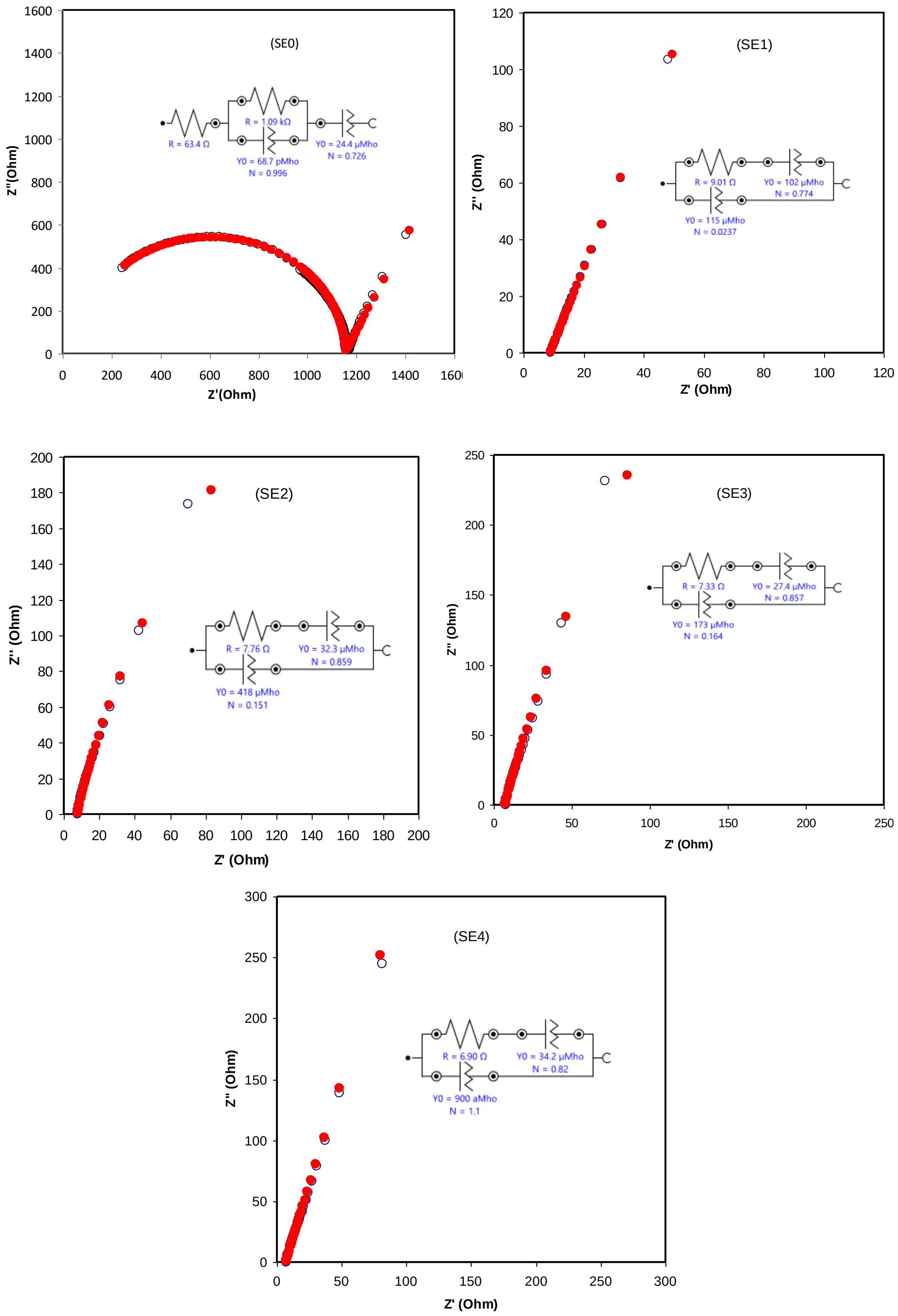

Figure 1. Impedance Nyquist plot (Z_i versus Z_r) of GPE surrounding temperature for (a) SE0, (b) SE1, (c) SE2, (d) SE3, and (e) SE4 systems. It is clear that the tail region rises and the semicircle at high frequencies disappeared for SE2-SE4 systems.

Initially, the Nyquist plot has shown two distinct regions that are; semicircle at the high-frequency region owing to bulk resistance of the polymers, and spike at the area of low frequencies because of the capacitance and resistance of charge transfer that formed at the electrode/electrolyte interface [30-35]. For the SE0 sample, the plot shows a semicircle because it is free from salts. However, a tail or spike is obtained by reason of a rise of the salt amount in the electrolyte. From the complex impedance plots, by extrapolating the spike to the real part (Z_r) at the higher intercept of a semicircle, the bulk resistance R_b for each SE GPEs was determined using equation (2) that among the imperfect semicircle and the tail [36-40].

It can be observed that the bulk resistance decreases with the increment of salt concentration to the system. Whereas; the ionic conductivity increases due to increasing the carrier's number in the electrolyte systems. This is as a result of the alteration in the mobile ions number in the GPEs along with the increment of dissociation of the salt that leads to the rising of conductivity. The equation of (2.4.1) shows that ionic conductivity is higher for lower bulk resistance value which means directly disproportional [41]. Moreover, the maximum ionic conductivity has found to be 4.755 x 10^{-2} S cm^{-1} for the 0.0012 mole composition of KSeCN salt at room temperature (listed in table 2) which indicates the highest ion mobility among the GPE systems.

In terms of comparison, the maximum ionic conductivity for the hydroxyl CS:$LiCF_3SO_3$:EC system was 2.75 x 10^{-5} S cm^{-1} reported by Wine [42]. For the PhCh-PEO-TPAI-EC system was 1.11 x 10^{-2} S Cm^{-1} examined by Buraidah [43]. For the system incorporated with CS:PEO:NH_4I:BMII has found to be 5.52 x 10^{-4} S cm^1[44]. The ionic conductivity of the above-mentioned systems has found to be lower than the current value, this is maybe due to their difference in the lattice energy of salts. The larger lattice energy amount leads to more difficult for the ions to dissociate.

Table 2. The DC ionic conductivity and dielectric constant values for all the GPEs with molarity difference at ambient temperature:

Sample code	Ionic conductivity σ_{dc} (S cm^{-1})	Dielectric constant
Se0	3.007 x 10^{-4}	1.10 x 10^{6}
Se1	3.590 x 10^{-2}	2.74 x 10^{8}
Se2	4.260 x 10^{-2}	5.10 x 10^{8}
Se3	4.433 x 10^{-2}	7.25 x 10^{8}
Se4	4.755 x 10^{-2}	1.30 x 10^{9}

3.2 Dielectric studies.

The key aim of the dielectric investigation is to illustrate the dielectric material capacity either it might store electric charges or not. In the meantime, the mechanism transfer of ions in the electrolyte systems can be estimated. Consequently, the current dielectric material is PhCh based GPEs. When it turns out the dielectric, there are two constituents contributed that are the dielectric loss and dielectric constant. The dielectric constant is the capability of a material to save electric charges, while dielectric loss is the energy waste to ions transport as well as for aligning the dipoles whereas the polarity of the electric field gets reversed swiftly, and generally associated to moving of charge carriers. The equations for the ε' and ε" are indicated in Eqs. (3) & (4) [24-29]. Figure (2) below shows the dielectric constant dissimilarity (ε′) versus frequency for the (SE0-SE4) gel electrolyte samples at room temperature. It is illustrious that the dielectric constant is large at low frequencies due to the impact of polarization. This occurs because of the charge carrier's gathering near the blocking electrodes [45-47]. The high value of dielectric constant leads to a large storing of the electric dipoles per-unit volume [48, 49]. At the same time, at large area of frequencies, the lower dielectric constant was observed, and it is ascribed to the relaxation mechanism domination. This phenomenon happened as a consequence of the quick changes in the field direction which results in inadequate time for the collection of ions at the electrodes [50-52]. Besides, the dielectric constant value was increased with the increase of the ratios of the salts. The reason for this is the reaction among the ions by the salt and the polar molecules that aid in the ion’s dissociation, consequently rise the charge carrier’s density in the backbone of the polymer [53]. For the dielectric loss plot in Figure (3), it demonstrates the similar manners as the dielectric constant. Though, dielectric loss demonstrates energy waste due to friction and scattering. This causes in the translational diffusion of ions, and orientation of dipoles to slow and fast in opposite directions, and develops heating impact over internal friction as heat energy [54].

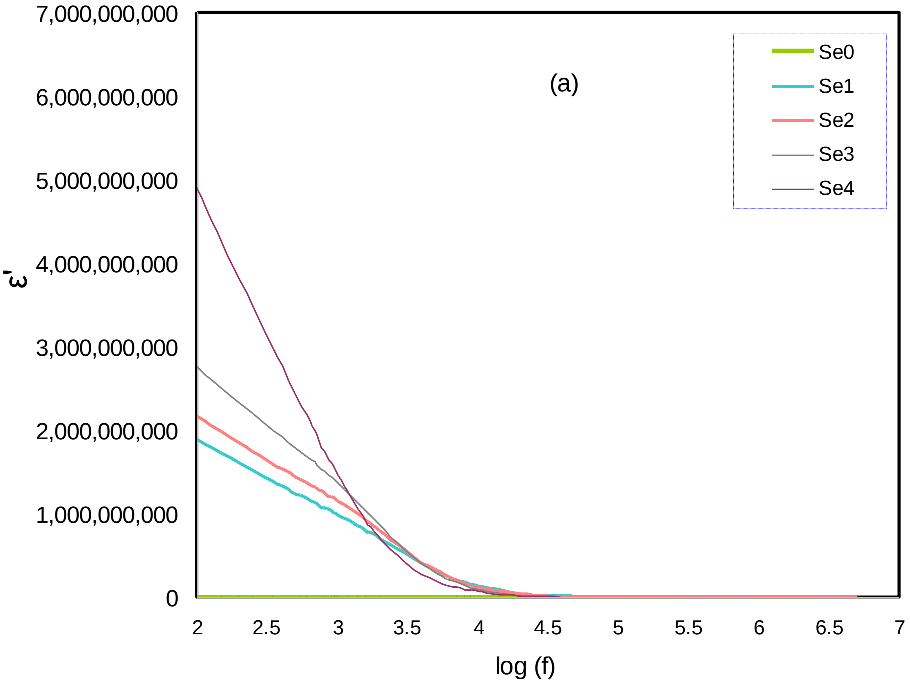

Figure 2. Dielectric constant (ε′) variation with frequency dependent of (SE0-SE4) gel electrolyte samples at ambient temperature. It is clear that ε′ increased for all the samples at low frequencies.

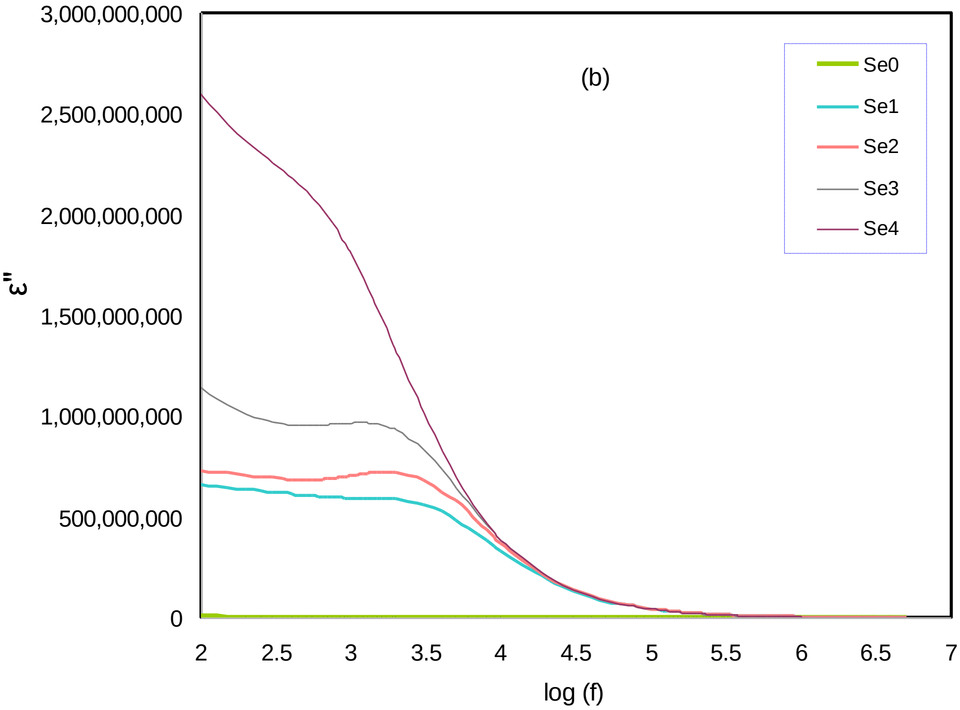

Figure 3. Dielectric loss (ε″) Variation with frequency dependent of (SE0-SE4) gel electrolyte samples at ambient temperature. It is clear that ε" increased for all the samples at low frequencies.

3.3. J – V characteristic of DSSC

The graph of the photocurrent density-voltage (J – V) of the DSSCs was performed for the characterization of PhCh-based GPEs with the various content of KSeCN salt. Figure 4 shows the obtained (J–V) graph of the DSSCs for the (SE0-SE4) GPE samples. Previous studies showed the lower or similar open-circuit voltage (V_{oc}), and higher short circuit density (J_{sc}) of the DSSCs with the liquid-based electrolytes than the DSSCs with the GPEs. In the DSSC with GPEs, this lower value of J_{sc} may attribute to the lower ion mobility than the LPEs [55]. From the J–V curve, the DSSC FF, and efficiency is computed using Eq. (5) and Eq. (6) respectively, and also the values of the J_{sc}, V_{oc}, fill factor (FF), as well as η%, are presented in table 3. It is clear that the incorporation of a modicum of the KSeCN salt in the system has enhanced the performance of the solar cell, and the value of the DSSC efficiency was significantly enhanced from 0.02% to 2.28% by addition of 0.0003 moles of the KSeCN salt. However, the efficiency increases with the increases of salt concentration refer to the additional electrons transport to the holes in the molecules of the dye. Nonetheless, the efficiency is reduced at a point because the increase of $SeCN^-$ ion amount contributes to the contact ion pairs rather than ions dissociation. The highest efficiency is 2.28% was obtained from the SE1 gel electrolyte sample which incorporated with 0.0003 moles of KSeCN salt, whereas, the minimum value was recorded for the GPE without adding salt [56-58]. The results revealed that both of the V_{oc} and FF of the DSSC are varied slightly, due to the cations which adsorbed on the external surface of TiO2 are affected by the location of the conduction bandgap [59]. On the basis of the J_{sc}, the sample SE2 indicates the greatest value. However, the J_{sc} value falls at some points due to ion pairs and aggregations. Therefore, the ions that act as transporter reduced.

Table 3. Parameters of DSSC of the GPEs with different molarity of the salt of KSeCN. The values of the J_{sc}, V_{oc}, FF, and η% are presented for all the samples.

Sample	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η%
Se0	0.27	0.37	0.22	0.02
Se1	6.19	0.61	0.6	2.28
Se2	8.65	0.29	0.68	1.68
Se3	8.36	0.63	0.21	1.13
Se4	1.33	0.54	0.45	0.32

In our previous works, it has been demonstrated that polymer electrolytes were extensively employed in solar cells and other applications for example photoelectrochemical, supercapacitors, as well as electrochromic devices [38-40, 60-62]. Table 4 shows the calculated efficiency (η%) for some systems reported in the literature. In comparison, the value of conversion efficiency of this work is close to some of these reports. Also, the cause why the KI efficiency is marginally larger in comparison with KSeCN is maybe because of the size of the ion of $SeCN^-$. The I^- ion size is significantly lower, which creates it to diffuse quicker, than the ion of $SeCN^-$.

Table 4. Various GPE based systems and their DSSCs efficiency (η%) values.

GPE systems	**Sensitizer**	**Efficiency (η%)**	**References**
PMA:LiI:TBP:I_2	N3	1.40	[63]
PEO:EC-PC-DMC:NaI:I_2	N719	3.6	[64]
PAN:NH_4I:I_2	N3	3.7	[65]
PMMA:PVA/LiI/MPII/PEG/I_2	N719	3.45	[66]
PVA:EC-PC-DMSO:KI-I_2	N719	2.74	[67]
PhCh:EC-DMF:KSeCN: $(SeCN)_2$	N3	2.28	This work

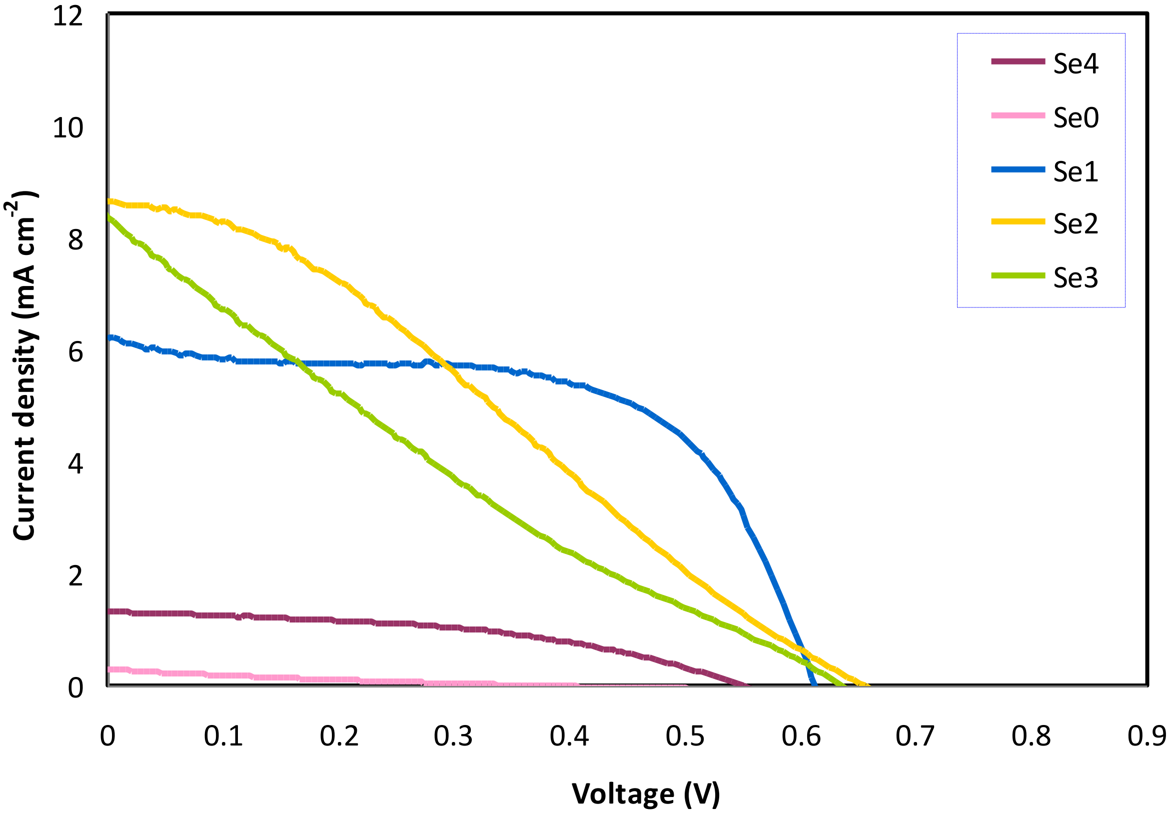

Figure 4. The J – V curve for the (SE0-SE4) GPE samples

4. CONCLUSION

In conclusion, a set of gel polymer electrolytes (GPEs) has been prepared successfully using PhCh as a host polymer, ethyl carbonate (EC) like a plasticizer, potassium selenocyanate (KSeCN) as a salt, and selenocyanogen as redox mediators to fabricate the dye-sensitized solar cells (DSSCs). The highest conductivity achieved in this project is 4.76 x 10^{-2} S cm^{-1} with the 0.012 moles of the KSeCN. From the dielectric studies, it was shown that the high concentration of ions leads to high conductivity. The GPEs were fabricated into DSSC and efficiency of 2.28% is obtained for the sample containing 0.0003 moles of the KSeCN salt. This is due to some factors such as lattice energy and the size of the anion. The result outcomes show that the PhCh-based GPEs have potential in the application of electrochemical devices.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support for this study from Ministry of Higher Education and Scientific Research-Kurdish National Research Council (KNRC), Kurdistan Regional Government/Iraq. The financial support from the University of Sulaimani and Komar University of Science and Technology are greatly appreciated. The authors would like to express gratitude to the University of Malaya for providing the research grant (RF021B-2018)

CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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