Polymer electrolyte system based on carrageenan-poly(3,4-ethylenedioxythiophene) (PEDOT) composite for dye sensitized solar cell

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Abstract. Poly(3,4-ethylenedioxythiophene) (PEDOT)-κ-carrageenan polymer electrolyte blend was prepared and incorporated as the electrolyte system in dye-sensitized solar cells (DSSC). Polymer blends prepared with different κ-carrageenan concentrations and molecular weights were investigated. It was found that the conductivity of the polymer blend increases with higher κ-carrageenan concentration, and lowers with degraded κ-carrageenan. The polymer blend was incorporated in a DSSC and yielded a solar cell with efficiency (η) of 0.421%.

1. Introduction
Dye-sensitized solar cells (DSSC) as next generation solar cells are promising alternatives to the conventional silicon-based solar cells owing to the low energy production requirement, low cost of raw materials, high configurational tunability and relatively good energy conversion efficiency [1].

The Gratzel configuration of the DSSC consists of a dye adsorbed on the surface of a nanocrystalline semiconductor oxide, an electrolyte solution and a platinum counter electrode all sandwiched between conductive glasses. This solar cell converts energy from sunlight through the photon excitation of the dye molecule ejecting electrons into the semiconductor oxide and to the external load. The ground state configuration of the dye molecule is regained by the donation of electrons from the electrolyte system through a redox process catalyzed by the platinum coating from the counter electrode [2].

The most efficient design of DSSC with 11% energy conversion employs an electrolyte system composed of the redox couple I-/I3− dissolved in volatile acetonitrile solvent [3,4]. However, its long term stability and performance is limited due to the use of low boiling liquid in the electrolyte system. To further improve DSSC for practical applications and commercial exploitation, studies have been done to replace the liquid system with other materials. Various materials studied for use in DSSC as alternatives to the liquid system includes room temperature ionic liquids [5-7] molten salts, organic and inorganic hole materials, and polymer electrolytes [8-13]. Among these alternatives, polymer electrolytes are attractive due to their unique hybrid network structure, negligible vapor pressure, high fabrication flexibility and thermal stability [14-17]. Moreover, using polymer electrolytes allow better

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electrode penetration, improving the long-term performance of the solar cell. Polymer electrolytes are composed of alkaline metal salts in a high molecular weight polymer with polar entities like amide, ether and ester linkages [18,19]. These electrolytes have been studied and employed in various devices such as separation membranes, solid-state batteries and solar cells [1].

One conductive polymer widely studied today for applications in various electronic devices is poly(3,4-ethylenedioxythiophene) (PEDOT). It is a very promising material due to its high conductivity, good stability, good transparency, low oxidation potential and low band gap. The ion diffusion properties of PEDOT are better compared to other conductive polymers. It has found applications as antistatic coating, electrical coating, supercapacitor, organic light emitting diode, biosensor and in photovoltaic applications [20,21]. The inclusion of other negatively charged polymers as dopant to the PEDOT matrix has been shown to improve its conductive properties as well as the electrochemical, optical, mechanical and transport properties of the PEDOT composite. The quality of the film was also observed to be better with polyelectrolyte dopants [22,23]. This study explores the use of naturally occurring κ-carrageenan as the negatively-charged polymer dopant to PEDOT for application in DSSC.

2. Materials and methods

2.1. Materials
EDOT (3,4-ethylenedioxythiophene) monomer was obtained from Aldrich, pure κ-carrageenan was obtained from Shemberg Corporation. Standard DSSC materials including FTO coated glass (TCO22-7), ruthenium dye-sensitizer (Ruthenium 535-bis TBA), TiO₂ semiconductor oxide (Ti-Nanoxide D11111) and platinum solution (Platisol 41121) were bought from Solaronix.

2.2. Preparation of PEDOT and PEDOT-κ-carrageenan blends
PEDOT was prepared using 0.01M EDOT in acetonitrile, and polymerizing the monomer with the addition of 0.02M FeCl₃ oxidant. PEDOT-carrageenan blends were prepared with the monomer EDOT, κ-carrageenan solution and FeCl₃ oxidant. Different concentrations of κ-carrageenan solution (0.5%(w/v), 0.2%(w/v) and 0.1%(w/v)) were used to investigate the effects of κ-carrageenan on the conductivity of the resulting PEDOT blends. To investigate the effect of the molecular weight of the dopant carrageenan on PEDOT, blends with degraded carrageenan were also prepared. The degraded carrageenan was prepared by dissolving 2g of κ-carrageenan in 100mL deionized water and was heated to 80°C. The pH of the carrageenan solution was adjusted to 12 from an original pH of 8.7 in the addition of 2M NaOH. The degradation process was then initiated by adding 20mL 30% H₂O₂ and left to degrade for 4 hours[24]. The resulting degraded carrageenan was collected by precipitating it with ethanol and drying in an oven. The average molecular weight of the resulting carrageenan was measured using GPC.

2.3. Polymer blend measurements
Cyclic voltammetry (CV) characterization was performed using a Powerlab/4SP Potentiostat to study the electrochemical behavior of the PEDOT-carrageenan blends. This was done by electrodeposition of the polymer on FTO glass at 1500mV for 210s in a three electrode chamber with the FTO glass as the working electrode, Ag/AgCl reference electrode and platinum counter electrode.

The electrodeposited polymer on FTO glass was then ran through the potentiostat to measure the CV properties of the polymers. A three electrode setup was also used with the Ag/AgCl reference electrode, platinum counter electrode and the deposited polymer as the working electrode. Measurements were obtained by running through CV with a scan rate of 100mV/s in a 4mM K₃[Fe(CN)₆] solution saturated in nitrogen.

Comparison of the PEDOT-carrageenan blend polymers with pure PEDOT was done by obtaining the infrared spectra of the polymers. This was carried out in a Nicolet 6700 FT-IR using KBr disc method. Differential scanning calorimetry (DSC), Perkin Elmer Differential Scanning Calorimeter
DTA7 with TAC7/DX Thermal Analysis Controller, was performed to record the glass transition temperature of PEDOT and the PEDOT-carrageenan blends. Around 10mg-20mg of samples were used for the measurements and were run from 35°C to 300°C. Conductivity measurements of the polymer blends were performed through the 4-point probe technique. The polymer deposited on the FTO glass was used for the tests. Samples were connected to the 4-point probe apparatus by wires attached to the surface of the sample.

2.4. DSSC fabrication and analysis
DSSC fabrication followed the traditional fabrication method. TiO₂ paste was placed and spread throughout the active area and was sintered at 450°C for 30 minutes. The photo anode was completed by immersing the FTO glass with the sintered TiO₂ in 3x10⁻⁴ M ruthenium (Ruthenium 535-bis TBA), solution in ethanol to allow the dye molecules to adsorb to the surface of the TiO₂ layer. The counter electrode was prepared by sputtering a layer of Platisol throughout the surface of the FTO glass. The counter electrode was then fired at 450°C for 10 minutes. The solar cell was completed by sealing the two electrodes and the electrolyte system was introduced into the solar cell. DSSCs prepared were evaluated under Abet Technologies AM1.5 solar simulator to determine the efficiency of the solar cell. The solar cells were illuminated under 100mV/cm² to get the voltage-current curve of the solar cell. From the I-V curve, the open circuit voltage (Voc), short circuit current (Isc) and fill factor (ff) were obtained to calculate the efficiency of the solar cell.

3. Results and discussion
3.1. Preparation of the PEDOT-carrageenan blends
The presence of counter ion dopant (e.g. PSS) for PEDOT establishes stability on the polymer. K-carrageenan with its well-spaced sulphate ester groups are potential polyelectrolyte dopant for PEDOT. Exploration of the blend between PEDOT and K-carrageenan has not been well studied.

To investigate the effect of the K-carrageenan molecular weight on the properties of PEDOT, the commercial carrageenan (MW_{av} = 6.4 x 10⁵) was degraded through oxidative degradation with hydrogen peroxide in alkaline condition. The hydroxyl radical attacks the glucosidic linkages in the carrageenan chain to afford the low MW carrageenan sample (MW_{av} =1.5 x 10⁴). The FT-IR analysis for the degraded K-carrageenan revealed peaks similar to the original K-carrageenan attributed to the absorbances of O-H (3427 cm⁻¹) and C-H (2955 cm⁻¹) bonds, polymer bound water (1644 cm⁻¹), sulphate stretching (1381 cm⁻¹), C-O-C bonds (1156 cm⁻¹) and C-O-S bonds (848 cm⁻¹) [25-26]. A pronounced reduction in the intensities of the glycosidic bonds (1072 cm⁻¹) can be observed owing to the degradation of the original K-carrageenan.

The original and the degraded carrageenans were blended separately with PEDOT through the oxidation of EDOT monomer in the carrageenan matrix to afford the composites. FTIR spectra of the resulting PEDOT-K-carrageenan blends were compared to pure PEDOT and pure carrageenan. PEDOT being an electrically conducting polymer showed no significant peaks owing to its conjugated nature undergoing geometric configuration [27]. Comparison of the spectra of the composite with the pure K-carrageenan shows shifts in peaks particularly the O-H stretching in carrageenan (3432 cm⁻¹) shifted to 3418 cm⁻¹ for the PEDOT-carrageenan blend. Notable differences in the C-O-C signals for both spectra can be observed. The C-O-C cyclic ester asymmetric stretching at the 1184 cm⁻¹ and the C-O-C α(1,3) linkage stretching at 700 cm⁻¹ for pure carrageenan were observed at a shorter frequency in the spectrum of the PEDOT-0.5% carrageenan blend. The bathochromic or red shift can be consistently observed for other PEDOT-carrageenan blends (PEDOT-0.2% carrageenan and 0.1% carrageenan), regardless of the carrageenan concentration. These results show the two polymer chains interacting as evidenced by the red shift of the O-H and C-O-C peak absorptions due of the increased solvation of the polymeric oxygen lone electron pairs thus forming extensive H-bonding in the presence of H₂O allowing better interaction between the PEDOT and K-carrageenan chains.
The FT-IR spectra of the PEDOT-degraded carrageenan blends were also compared with the spectrum of the degraded pure carrageenan to confirm the PEDOT blend formation. Similar observations were noted comparing the pure degraded k-carrageenan with the blue-colored composites of PEDOT containing varying % of degraded carrageenan (0.5%, 0.2%, 0.1%) indicating the interactions of the polymer chains in the formation of the blend. These observed bathochromic shifts of the OH and C-O-C absorptions are due to the interactions between the PEDOT chains and degraded carrageenan blends suggesting physical entanglements between polymer chains.

3.2. Surface morphology and elemental analysis
Surface morphology characterization of the chemically and electrochemically prepared samples was determined through SEM analysis (Figure 1).

![Figure 1](image1.png)

**Figure 1.** SEM image of pure PEDOT film prepared (a) chemically and (b) electrochemically deposited on FTO glass.

The surface of chemically prepared PEDOT (Fig. 1a) showed defined shapes with microparticle deposits while PEDOT electrodeposited on FTO glass at 1500mV (Fig 1b) showed a formation of blob with thread-like deposits of PEDOT. The observed difference in the surface morphology is due to the different modes of polymerization resulting to their differences in morphologies. Figure 2 shows the SEM images of carrageenan and the PEDOT-carrageenan blends prepared electrochemically.

![Figure 2](image2.png)

**Figure 2.** SEM Images of (a) pure carrageenan, (b) PEDOT-0.1% carrageenan, (c) PEDOT-0.2% carrageenan and (d) PEDOT-0.5% carrageenan electrochemically deposited on FTO glass.

The SEM image of pure carrageenan (Fig. 2a) shows a smoother surface compared to the electrochemically prepared PEDOT (Fig 1a). The PEDOT-carrageenan blends (Fig. 2-b-d) showed more similar surface morphology with pure k-carrageenan than the pure PEDOT, where smaller,
grain-like deposits can be observed. Although the surface morphologies of the blends are similar to pure carrageenan, the presence of the blue color of the blends confirm the presence of PEDOT in the carrageenan matrix. The SEM images of the chemically prepared PEDOT-carrageenan blends (Fig. 3.7) were observed to have similar surface morphologies with each other, having fine particles on the surface. Comparing both methods, the electrochemical method yielded a film with smoother surface because of the controlled conditions applied equally throughout the film.

The SEM images of the composite consisting of PEDOT and degraded carrageenan in 0.1%, 0.2% and 0.5% concentrations (Fig. 4) were observed to have similar surface morphologies with the PEDOT-carrageenan blends, indicating that the incorporation of κ-carrageenan, whether degraded or not degraded, alters the film formation of PEDOT. The effect of adding whether the original or degraded carrageenan yielded a PEDOT-carrageenan blend with the same surface morphology.

EDX analysis was also performed on the electrodeposited polymer samples to look at the elements present in the polymer samples to confirm the deposit of polymer. The EDX analysis of both the PEDOT-carrageenan and PEDOT-degraded carrageenan blends yielded the expected C, O and S elements.

3.3. Conductivity measurements
Conductivity of the polymer blends were tested to identify which blend would be the most conductive for incorporation into a dye-sensitized solar cell. Conductivity was determined through the four-point probe Van der Pauw method and through cyclic voltammetry (CV). Through the Van der Pauw method, the conductivity of the polymers was determined by measuring the voltage at constant current.
of 12 mA and measuring the thickness of the polymer film through SEM. The resulting conductivity was obtained by first calculating the resistivity of the film using equation (1) then the conductivity was calculated using equation (2). Table 1 shows the conductivity results.

$$s = \frac{\pi d}{\ln 2} \left( \frac{V_1}{I_1} + \frac{V_2}{I_2} \right) f \left( \frac{R_1}{R_2} \right)$$  \hspace{1cm} (1)

$$\rho = \frac{1}{s}$$ \hspace{1cm} (2)

**Table 1.** Conductivity of PEDOT and PEDOT-carrageenan blends.

| Sample                   | $V_1$  | $I_1$  | $V_2$  | $I_2$  | Thickness (cm) | Conductivity (S/cm) |
|--------------------------|--------|--------|--------|--------|----------------|---------------------|
| PEDOT                    | 2.414  | 12.11  | 1.595  | 12.14  | 6.50E-05       | 10.42               |
| PEDOT-0.1% carrageenan   | 5.439  | 12.21  | 1.255  | 12.20  | 5.14E-05       | 9.24                |
| PEDOT-0.2% carrageenan   | 6.139  | 12.18  | 1.380  | 12.13  | 3.10E-05       | 13.61               |
| PEDOT-0.5% carrageenan   | 2.163  | 12.11  | 1.524  | 12.11  | 4.51E-05       | 16.23               |
| PEDOT-0.1% degraded carrageenan | 7.030  | 12.08  | 1.580  | 12.10  | 5.38E-05       | 6.85                |
| PEDOT-0.2% degraded carrageenan | 4.319  | 12.03  | 3.486  | 12.05  | 4.18E-05       | 8.20                |
| PEDOT-0.5% degraded carrageenan | 3.555  | 12.10  | 2.298  | 12.10  | 5.04E-05       | 9.17                |
| k-carrageenan            | -      | -      | -      | -      | -              | 3.149               |

PEDOT was observed to have a conductivity of 10.42 S/cm, consistent to literature conductivity [28]. Generally, the conductivities of the PEDOT-carrageenan blends were observed to be higher than the PEDOT-degraded carrageenan blends. The most conductive blend is the PEDOT-0.5% carrageenan composite exhibiting 16.23S/cm conductivity, which was higher than the conductivity of the electrically conducting pure PEDOT and pure κ-carrageenan. The conductivity of the polymer blends was seen to be related to the concentration of carrageenan, where by increasing the concentration of carrageenan increases the conductivity of the polymer blend.

CV measurements were also performed to look at the redox behavior of the polymers (Figure 5).

**Figure 5.** CV cycles of (a) PEDOT-0.1% carrageenan, (b) PEDOT-0.2% carrageenan and (c) PEDOT-0.5% carrageenan from -800mV to +800mV.
The CV cycles of PEDOT-carrageenan blends showed the reversible property occurring between the -800mV to +800mV range. The peak currents of the cycles were also seen to increase as the concentration of carrageenan increased, with the PEDOT-0.5% carrageenan blend having a cycle with the highest $I_{pa}$ and $I_{pc}$ values. This trend was observed to be consistent with the conductivities measured by the four-point probe method, since the peak currents of the PEDOT-carrageenan blends increased as concentration increased showing the PEDOT-0.5% carrageenan blend as the most conductive.

The CV profile of the PEDOT-degraded carrageenan blends on the other hand showed very narrow cycles and only the PEDOT-0.5% degraded carrageenan sample had an observable redox cycle. The differences in the conductivities and redox behavior of the PEDOT-carrageenan blends and the PEDOT-degraded carrageenan blends could be attributed to the ability of the long carrageenan chains to keep excess solvent in its matrix increasing its ability to transport ions. It has been observed that gelation of κ-carrageenan does not occur below a certain critical molecular weight[29]. The concentration of the polysaccharide also affects the conductivity and redox behavior of the blend. The relationship between the concentrations of the polysaccharide; increasing the concentration of the conducting polysaccharide increases conductivity, was consistent with the literature [30].

### 3.4. Thermal analysis

Thermal analysis of PEDOT and the PEDOT-carrageenan blends(Table 2) showed a general observation that incorporation of carrageenan to PEDOT increase the glass transition temperature ($T_g$). This is due to the incorporation of a high molecular weight polymer chain to PEDOT, which stiffens the PEDOT chain causing the $T_g$ to increase.

| Sample                      | $T_g$ (°C) |
|-----------------------------|------------|
| PEDOT                       | 64.431     |
| PEDOT + 0.1% carrageenan    | 85.207     |
| PEDOT + 0.2% carrageenan    | 77.683     |
| PEDOT + 0.5% carrageenan    | 72.748     |
| PEDOT + 0.1% degraded carrageenan | 79.475     |
| PEDOT + 0.2% degraded carrageenan | 83.116     |
| PEDOT + 0.5% degraded carrageenan | 93.618     |

The decreasing trend of the observed $T_g$ of the PEDOT-carrageenan blends as the concentration of κ-carrageenan increased can be attributed to the ability of the long chains-carrageenan polymer to trap water molecules into its matrix to form a gel, making the chains more fluid. The $T_g$ of the PEDOT-degraded carrageenan composites, on the other hand, had an opposite trend, which can be attributed to the molecular weight of the degraded carrageenan. A study previously done by Souza, H. et al. [29] showed the relationship of the thermal properties of κ-carrageenan with the molecular weight. They were able to show that the gel forming property of κ-carrageenan is dependent on the molecular weight of the polysaccharide; below a certain critical molecular weight (MW ≈ 3.0x10^5), no κ-carrageenan gels are formed. Due to the limited ability of degraded carrageenan to form gels, it would not be able to keep water in its matrix efficiently resulting to a more rigid polymer system, higher $T_g$.

### 3.5. DSSC measurements
Considering the conductivity and CV observations, the best candidate for the polymer electrolyte blend to be incorporated in DSSC is the PEDOT-0.5%carrageenan blend. The fabrication of the DSSC follows the protocol described by Solaronix [31]. The PEDOT-0.5%carrageenan blend was introduced as a gel and sandwiched with the counter electrode and the anode assembly. This is referred in this study as unsealed DSSC. Another protocol, where the sides of the cells were sealed with the 100μm thick film sealant and the PEDOT-0.5%carrageenan gel was introduced through a hole previously made on the counter electrode. The hole was further sealed with the thermoplastic sealing material and a piece of glass to afford a sealed DSSC.

Efficiency of the solar cells employing the electrolyte system was evaluated by irradiating under 100mW/cm² AM 1.5G light source. A DSSC with the traditional iodide/triiodide liquid system was likewise prepared as a standard. The I-V curves of the DSSCs are shown in Figure 6.

From the I-V curves, $V_{oc}$, $I_{sc}$ and fill factor were determined (Eqn. 3) and the efficiencies of the solar cells were calculated (Eqn. 4) (Table 4).

$$\eta = \frac{V_{oc} \times I_{sc} \times ff}{P_{in}}$$

Table 4: DSSC efficiency data.

| Electrolyte System          | $V_{oc}$ (V) | $I_{sc}$ (mA) | $ff$  | $\eta$ (%) |
|-----------------------------|-------------|---------------|-------|------------|
| PEDOT-carrageenan (Sealed)  | 0.565       | 3.37          | 0.221 | 0.421      |
| PEDOT-carrageenan (Unsealed)| 0.439       | 2.19          | 0.259 | 0.249      |
| Iodide-triiodide (Sealed)   | 0.724       | 17.36         | 0.631 | 7.93       |
| Control                     |             |               |       |            |

The DSSC employing the traditional liquid electrolyte system had an efficiency of 7.93% which is consistent with the literature (efficiency range between 7-11%). The DSSC with the polymer blend as electrolyte system was observed to have a very low efficiency of less than 1%. This low efficiency can be attributed to the very stiff configuration of PEDOT in the electrolyte system. Because of the stiffness of the PEDOT chains, electron transport is not as efficient compared to the liquid system, as seen from the $I_{sc}$ values, where the cell with the liquid electrolyte recorded greater $I_{sc}$ values than the PEDOT-carrageenan cell. The fill factors of the PEDOT-0.5%carrageenan DSSC were also lower than the $I/I_3$ system. The low fill factor of the DSSC shows the high resistance of the system leading to...
internal loss of the current produced by the solar cell. Comparing the DSSC with literature employing various polymer electrolytes yielded DSSC with varying efficiencies ranging from PEO system with 0.01% efficiency [32] to PEPI-EO with an efficiency of 5.3% [33].

The electrolyte activity of the PEDOT-carrageenan system is based on the redox action of PEDOT, which in the presence of the carrageenan polymer matrix, undergoes charge hopping mechanism by the self-exchange of charges between the redox couple. However, basing from the CV data and molecular modeling, there is an observed preference for the reduced form of PEDOT such that the process is not 100% reversible. The CV peak current ratio in the PEDOT-0.5% carrageenan blend is slightly less than unity indicating that only some fraction of the reduced PEDOT in the forward scan are available for reoxidation on the reverse scan. There is in effect a kind of barrier that prevents efficient charge hopping mechanism. Inside the DSSC, various reactions are going on in the pico-second and millisecond scale that interferes with the forward process of electron flow. Changing the electrolyte system specifically affects the dye regeneration process and the redox process. A stiff polymer electrolyte system although conductive, limits the ionic mobility, lowers the rate at which the electrons could be used by the excited dye and decreases overall conversion in the solar cell.

4. Conclusion
Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly conductive polymer electrolyte utilized for many purposes; and conductivity improved with the addition of dopants. In this study, the natural polysaccharide κ-carrageenan was used as dopant and incorporated into PEDOT producing a more conductive polymer material. Increasing the concentration of κ-carrageenan resulted to an increase in the conductivity of the PEDOT-carrageenan blend. The utilization of a lower molecular weight carrageenan and using it as the dopant electrolyte causes the conductivity to decrease due to its inability to efficiently trap water in the polysaccharide matrix, resulting to a highly crystalline polymer material. The PEDOT-carrageenan blends, as polymer electrolyte systems in dye-sensitized solar cells show low efficiency in converting solar energy to electrical energy.

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