PEO based polymer composite with added acetamide, NaI/I₂ as gel polymer electrolyte for dye sensitized solar cell applications

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Abstract. Poly (ethylene oxide) (PEO) based gel polymer electrolytes (GPEs) with added acetamide, NaI/I₂ have been prepared for dye-sensitized solar cells application (DSSC). The Dye-sensitized solar cell investigated the performance of the optimized gel polymer electrolyte. GPEs synthesized by adding up of acetamide with different wt% in poly (ethylene oxide) (PEO) and poly (ethylene glycol) dimethyl ether (PEGDME) with NaI/I₂. A maximum power conversion efficiency of 5.92% is achieved for PEO/PEGDME with 10 wt% acetamide in the photovoltaic performance under 100 mW/cm² illumination and it exhibits maximum ionic conductivity (σ = 2.81×10⁻³ S/cm) among all electrolytes, compared to PEO without acetamide (η = 4.35%). The gain in open circuit voltage (Vₜ₉) was observed for GPEs due to the decrease in the recombination effect and electron lifetime increases by the addition of acetamide on the PEO. The fill factor (FF) is increased due to the growth in the ionic conductivity and amorphous nature of the GPE increases by the addition of acetamide on the PEO.

1. Introduction:
Investigate gatherings are concentrating on finding new sustainable power sources to accomplish overall energy requirements towards increasing population and emergent technology. Grätzel created a dye-sensitized solar cell (DSSC) in 1991 and delegated as 3rd generation solar photovoltaics [1]. The efficiency of DSSCs announced as high as ~13% and working process as like the rule of plant photosynthesis [2]. However, DSSC still has few issues such as unstable nature of organic solvents and combustible, stability issues because of the degradation of dyes in the photoanode, corrosion of counter electrode and severe leakage and sealing issues in pragmatic applications [3]. Along these lines, numerous specialists have been set up to substitute the liquid electrolyte by organic based materials [4, 5], ionic liquids [6, 7], solid polymer electrolytes [8, 9] and gel polymer electrolytes [10-12].

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Nevertheless, unfortunately, DSSCs made with solid polymer electrolytes (SPEs) shows very low efficiency (4%) [13] due to their low ionic conductivity [14,15]. To beat this issue, gel polymer electrolytes (GPEs) newly introduced. Even though, the higher efficiency of GPEs and a considerable stability, their efficiency values are still lower than that of liquid electrolytes. Consequently, various endeavors made to build the cell performance of DSSCs containing GPE by utilizing different polymers, biopolymers, and additives, for example, nanofillers and plasticizers [16, 17]. Specifically, the addition of plasticizer provides to reduce crystallinity and gives free space to ionic mobility for GPE [18]. De Paoli et al. assembled first DSSC by using a copolymer of poly (epichlorohydrin-co-ethylene oxide) and poly (o-methoxy aniline) with NaI/I$_2$ based electrolyte [19]. A quasi solid state DSSC, with PEO/P(VDF-HFP) complex polymer using acetamide with SiO$_2$ nanoparticles, KI/I$_2$ was made up by Cui et al. revealed photovoltaic conversion efficiency (PCE) of 6.04 %[20]. The witnessed efficiencies in the literature, reports are sensibly little for made-up of DSSCs with solid polymer electrolytes (SPE) because of its unfavorable ionic conductivity in the polymer system, poor crystallinity could bring about the drop of PCE. Hence, a significant report focused on improving the efficiency of DSSC with GPEs [21, 22]. A recent report by Pavithra et al. revealed the PCE of 9.01 % by GPEs consisting with Poly (ethylene oxide)-acetamide composite [23]. Chen et al. achieved 9.5% efficiency using of Poly (acrylonitrile-co-vinyl acetate) (PAN-VA) and TiO2 nanofiller [24].

In this paper, a sequence of GPEs by the addition of different wt% of acetamide as a plasticizer in PEO/PEGDME polymer matrix and NaI/I$_2$ redox couple are prepared. Among frequently utilized polymers, poly (ethylene oxide) is one of the best polymers broadly utilized as polymer electrolyte because of its excellent solvation and chemical stability. In any case, PEO has semi-crystalline nature at room temperature and reductions its ionic conductivity that confines its useful applications [25]. A liquid oligomer (i.e., Poly (ethylene glycol) dimethyl ether) is blended to PEO to improve the ion mobility and diffusion of electrolyte through the mesoporous of a TiO$_2$ based photoelectrode. Acetamide is utilized as a plasticizer and it has two important groups: one carbonyl group present in the nitrogen atom and another one in the oxygen atom. The -NH$_2$ groups cooperate with PEO to form polymer complexation with fascinating electrochemical properties [23]. The conformational changes in the acetamide altered GPE are examined utilizing FTIR, DSC, XRD and SEM. The ionic conductivity and temperature dependence of ionic conductivity were resolved. At long last, DSSCs are assembled utilizing the acetamide altered GPEs and described by solar simulator under 100 mW/cm$^2$ illumination to a measured efficiency of the cell.

2. Experimental:

2.1 Materials:

Poly (ethylene oxide) (PEO, $M_w = 10^6$gmol$^{-1}$), Poly (ethylene glycol) dimethyl ether (PEGDME, $M_w = 250$gmol$^{-1}$), Acetamide, LiI, Iodide (I$_2$), N719 and FTO covered glass from Sigma-Aldrich, acetonitrile (Merck), Titanium dioxide (TiO$_2$, Dyesol), platinum solution (Solaronix) were purchased.

2.2 Preparation of Polymer Gel Electrolytes:

GPEs were set up by including 0.5 g of poly (ethylene oxide) (PEO) in a mix of acetonitrile and Poly (ethylene glycol) dimethyl ether (PEGDME) under nonstop mixing for 2 hours. To this blend around 0.2 g of NaI, 0.08 g of I$_2$ and different wt% of acetamide (0%, 5%, 10%, 20%) were blended and stirring has proceeded for an extra 2 hours. The prepared electrolyte solution continued stirring during the night. Therefore, such homogenous solution heated at 80 °C to dissipate acetonitrile and to yield gel polymer electrolyte. For all GPEs, the concentration ratio kept up at 0.4 for the iodine salt and iodide [NaI/ I$_2$]. A sequence of gel polymer electrolytes (A: PEO + NaI+ I$_2$, B: PEO + PEGDME + NaI + I$_2$, C: PEO + PEGDME + 5 wt% Acetamide+ NaI + I$_2$, D: PEO +PEGDME + 10 wt% Acetamide + NaI + I$_2$, E: PEO + PEGDME +20 wt% Acetamide + NaI + I$_2$) were synthesized.
2.3 Fabrication of dye sensitized solar cells:
DSSCs were fabricated following the procedures identified in the literature [26]. Briefly, as mentioned below:

2.3.1. Preparation of photo electrodes:
Fluorine doped SnO\(_2\) (FTO) covered glass substrates are washed by a delicate detergent solution taken after by deionized water, acetone and 2-propanol in an ultrasonic shower. A smaller TiO\(_2\) blocking layer was deposited onto the surface of cleaned FTO by treat with 40 mM TiCl\(_4\) solution at 70 °C for 30 min, cleand with deionized water. Nanocrystalline titanium dioxide (TiO\(_2\), Dyesol) transparent layer was secured onto TiCl\(_4\) treated FTO glass substrate, repeated the procedure to accomplish 12 μm thick TiO\(_2\) film. Further, 4 μm thick film of scatter TiO\(_2\) (Dyesol) is coated, sintered at 500 °C for 30 min. TiCl\(_4\) treatment was performed at 70 °C for 30 min to upgrade the surface area of TiO\(_2\). These electrodes are dipped in the N719 dye solution (0.3 mM) for 18 hr under dark condition. The obtained photo electrodes were rinsed twice by absolute ethanol to expel any unanchored dye molecules, finally dried under nitrogen purge.

2.3.2. Preparation of counter electrodes:
spin coating technique is utilized to prepare counter electrodes. Briefly, cleaned FTO substrates were located on the substrate holder of spin coater and a 40 μl of platinum solution (Solaronix) was dispensed and rotated of 5000 RPM for 30 sec, followed by sinter at 500 °C for 15 min.

2.3.3. DSSC Assembling:
Test cells were assembled by utilization of 60μm thickness polymer film, which was located between the counter electrodes and photo electrodes, and the developed polymer gel electrolytes were filled in the middle. The assembled DSSC have an active area of 0.16 cm\(^2\).

2.4 Characterizations:
The structural properties of GPE were done by Philips: PW1830 X-ray diffractometer. BRUKER FT-IR Spectrometer measured Fourier transform infrared spectra (FTIR) of the GPEs. Surface morphology was obtained by Hitachi Model S-3400 SEM instrument. DSC thermograms were studied at the heating rate of 10 °C min\(^{-1}\) with help of a Mettler-Toledo DSC1 instrument. The conductivity of the GPEs was studied by Broadband dielectric spectroscopy (BDS). Current density-Voltage (J-V) characteristics were done with the PEC-L01 solar simulator (Paccell Inc.) associated to source meter (2401, Keithley). The simulator was adjusted with standard Si cell to get 100 mW/cm\(^2\) output powers (1 Sun condition). Broadband dielectric spectroscopy (BDS) studies were conducted by use of NOVOCONTROL in the frequency range of 1 Hz to 1 MHz.

3. Results and discussion:
In order to identify modifications in the polymer chain, GPEs were analyzed by FTIR, DSC, XRD and SEM results and how such compliance change may follow up on the ionic conductivity was examined. Finally, how these factors influenced on ionic conductivity of GPEs was verified and the obtained results were compared with impedance studies.

3.1 Fourier transforms infrared spectroscopy:
FTIR is useful to give data on the chain formation of polymers and the presence of collaborations among the segments in PEO based electrolyte [27]. FT-IR spectra of the GPEs appear in figure 1. The-stretching vibrations of -CH\(_2\) in PEO happens at 2871 cm\(^{-1}\) because of the cooperation of sodium-ion and acetamide with a polymer in GPE and intensity of this peak diminishes [28]. These progressions of -CH\(_2\) confirms the coordination amongst PEO and acetamide. Additionally, a peak identified due to C-O-C stretching vibrations at 1106 cm\(^{-1}\) in PEO chain [29]. For GPEs containing acetamide, this peak
gets broad and the intensity reduced by the supply of acetamide substance up to 10 wt%. In the meantime, the peak appeared at 1340 cm\(^{-1}\) due to the characteristic of the crystallized PEO gets sharpened and the intensity also reduced upon supply of acetamide substance up to 10 wt%. Acetamide has two important groups: one carbonyl group present in the nitrogen atom and another one in the oxygen atom. The C=O group in carbonyl can synchronize effectively with the polymer matrix in the GPE through sodium ion while the polar -NH\(_2\) group have a single pair of electrons will cooperate through the iodide ions in the redox couple. The absorption peaks of acetamide were observed due to the presence of –NH\(_2\) and –C=O groups at 1659 cm\(^{-1}\) and 3460 cm\(^{-1}\) respectively [23].

![Figure 1: FTIR spectra of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide)](image)

3.2 Differential Scanning Calorimetry:
Differential scanning calorimetry (DSC) is broadly applied to examine the phase modulation of the gel polymer electrolytes. The DSC thermograms appear in figure 2 containing a different wt % of acetamide in GPE. The flexibility of the polymer can be clarified by one of the imperative parameters know as glass transition temperature (Tg)[30]. The Tg estimations of various wt % of acetamide in GPE are given in the Table-1. By the addition of acetamide, Tg decreases up to PEO/PEGDME with 10 wt% of acetamide. This demonstrates that the increase in the amorphous nature and increment free volume of the GPE by the addition of acetamide, as a result mobility of the ions is improved which indicates that the ionic conductivity of GPEs also increases [31]. Further, the adding of acetamide over 10 wt% shows a decrement in Tg which shows excessively of acetamide may decrease the free volume and flexibility in the polymer matrix. In this manner, such changes in Tg may impact the ionic conductivity and activation energy [32].

3.3 Structural properties:
The X-ray diffraction studies provide probable influence on PEO of semi crystalline phase by adding acetamide content. X-ray diffraction pattern of GPEs with various wt% of acetamide are shown in figure 3. Pure PEO is a semi crystalline polymer and exhibits two strong crystalline peaks at 19.1\(^\circ\) and 23.2\(^\circ\) [33]. PEO with 0 wt% of acetamide (sample A) shows some semi crystalline peaks and remains all GPEs show amorphous nature. The XRD pattern shows only one broad peak appeared at 22.62 \(^\circ\), which indicates the variation in the crystalline phase of gel polymer electrolytes. The diffraction peaks become broad up to PEO/PEGDME with 10 wt% acetamide content is inserted in the polymer complexes. Hence, it can suggest that the PEO undergoes significant structural reform while blending and thus complexation occurs in the amorphous phase. It has been reported that ion mobility is better in the amorphous phase because their mobility is helped by polymer segmental motion [34]. Among all GPEs, PEO/PEGDME with 10wt% acetamide shows wide and less intensity curve, which exhibits high amorphous nature compare to others.
Figure 2: DSC thermograms of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide)

Figure 3: X-ray diffraction pattern of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide)

3.4 Scanning electron microscopy:
SEM image of GPEs with different wt% of acetamide are displayed in the Figure 4. SEM images of GPE (Figure 4a-b) demonstrate a broke layer structure yet GPE containing PEO/PEGDME with 10 wt% of acetamide[35]. Figure 4d demonstrate a fibrous unbreakable structure due to the interaction of acetamide with the ether oxygen in PEO and images revealed that the redox couple bound inside the walls of the gel structure establishes a homogeneous allotment [23]. SEM images of GPE (Figure 4c-e) show tiny gaps between the layers in GPE by a blend of acetamide. In this manner, a blend of acetamide gives impressive adjustments in the surface morphology and increment in the free volume of the GPE that makes development in the ionic conductivity [36].

3.5. Ionic conductivity of gel polymer electrolytes:
In DSSC, the improvement in mobility of the redox couple and ionic conductivity of the GPE provides better power conversion efficiency [37]. Figure 5 indicates complex impedance plots (Z’ vs Z”) for GPEs with different wt% of acetamide. In the complex impedance plots, bulk resistance (R_b) was measured by extrapolated intercepts on the Z’ of the common part of two arcs. Therefore, the ionic conductivity of the prepared GPEs is measured by bulk resistance (R_b) values acquired in Broadband Dielectric Spectroscopy (BDS) by applying the formula [38]:

\[ \sigma = \frac{l}{AR_b} \]  

(1)

Where ‘A’ is the area, ‘l’ is the space between two electrodes and ‘R_b’ is the bulk resistance measured from BDS spectrum. From Table-1 it is resolved that the ionic conductivity of GPE maximum for PEO/PEGDME with 10 wt% acetamide. It is broadly speaking that ionic conductivity is large in the amorphous phase of GPE [39]. Upon addition of acetamide, Ionic conductivity is increased; this is because of the decrease of crystallinity of the GPE and because of the collaboration of acetamide with
PEO. A further blend of a large amount of acetamide may decrease the free volume and flexibility in the polymer system that indicates a decrement in ionic conductivity.

![Figure 4: Scanning electron microscope images of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide).](image)

The temperature variation (25°C–60°C) of the ionic conductivity of GPEs with different wt% of acetamide is shown in Figure 6. The flexibility and free volume in the GPE increase with an increase of temperature and hence enhances the mobility of ions in the polymer systems [40]. As can be seen, the ionic conductivity increments incredibly at the melting temperature of PEO (60°C), which shows that the electrolyte has turned out to be completely amorphous [27]. Therefore, the Arrhenius equation is used to demonstrate the temperature-conductivity performance of the GPEs [41]:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right)$$  \hspace{1cm} (2)

Where $\sigma_0$ is a pre-exponential factor, $E_a$ is activation energy for ionic mobility, $K$ is Boltzmann constant and $T$ is the absolute temperature in Kelvin scale. The activation energy ($E_a$) values evaluated from the Arrhenius equation and tabulated in Table-1 for various samples. From figure 6, the ionic conductivity was observed to increase with increasing temperature and GPEs are easily expand as temperature increases hence creating more free volume [42]. The results clearly illustrate that the adding of acetamide to electrolyte can reduce the activation energy of redox couple. In fact, lower $E_a$ is liable for higher ionic conductivity in correlation with pure PEO based GPE. This is mostly due to the amorphous phase of the polymer matrix, which will helpful for ion mobility [43].
3.6 Photovoltaic performance of the DSSCs:
DSSCs assembled to determine the performance of prepared GPEs potentiality in a practical application. The photovoltaic characteristics of the DSSC using gel polymer electrolytes with different wt% of acetamide are shown in Figure 7 and the results are tabulated in Table 1. The performance parameters of all DSSC such as open circuit voltage $V_{oc}$ (V), short-circuit current density $J_{sc}$ (mA/cm$^2$), fill factor (FF) and power conversion efficiency $\eta$% were obtained with different gel polymer electrolytes. The fill factor (FF) was calculated using:

$$
FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}}
$$

(3)

Where $V_{max}$ and $J_{max}$ are the voltage and current density at the maximum power output point.

The power conversion efficiency $\eta$ was calculated

$$
\eta \% = \frac{V_{oc} \times J_{sc} \times FF}{Total\ incident\ light\ power\ density} \times 100
$$

(4)

Figure 7. Reveals the voltage-current density (V-J) characteristics of DSSCs by platinum electrodes under solar simulator irradiation of 100 mW/cm$^2$ (AM 1.5). The power conversion efficiency of Cell-D shows superior in a performance of $\eta = 5.92$ %, $J_{sc} = 13.91$ mA/cm$^2$, $V_{oc} = 0.70$ V and FF = 0.60, which indicates the GPE with 10% acetamide having good potentiality than the other electrolytes, reflects the enhanced DSSC performance. However, for higher wt% of acetamide, the photocurrent conversion efficiency values reduce due to the complex formation between $I_3^-$ and acetamide which may decrease the ionic conductivity ($\sigma$). Consequently, photocurrent conversion efficiency reduces for 20% wt of acetamide. Considering the favorable high conductivity of GPE with 10% acetamide, the platinum CE can exhibit the improved efficiency. A systematic study is conducted to assessment the acetamide and PEGDME loads in GPE and shown in Figure 7. The conversion efficiencies of DSSCs with different acetamide concentrations are 4.35 %, 4.67 %, 5.58 %, 5.92 % and 5.13 % for Cell-A, Cell-B, Cell-C, Cell-D and Cell-E respectively and the other photovoltaic parameters are evaluated from the J-V characteristic are given in Table-1.

![Figure 5: impedance spectra of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide)](image1)

![Figure 6: Temperature dependence of ionic conductivity of GPEs (A, B, C, D and E represents PEO/PEGDME with different wt% of acetamide).](image2)
Table-1: Gel polymer electrolyte parameters and Photovoltaic cell parameters of fabricated test cells.

| Gel Polymer Electrolyte | Glass transition temperature \( T_g \) (°C) | Ionic Conductivity \( \sigma \) (mS/cm) | Activation Energy (eV) | \( V_{oc} \) (V) | \( J_{sc} \) (mA/cm\(^2\)) | Fill Factor | Efficiency \( \eta \) (%) |
|-------------------------|---------------------------------------------|------------------------------------------|------------------------|----------------|--------------------------|-------------|--------------------------|
| A                       | -45.06                                      | 1.67                                     | 0.1320                 | 0.67           | 16.70                    | 0.38        | 4.35                     |
| B                       | -50.11                                      | 2.23                                     | 0.0715                 | 0.66           | 14.65                    | 0.48        | 4.67                     |
| C                       | -51.43                                      | 2.49                                     | 0.0619                 | 0.69           | 15.74                    | 0.51        | 5.58                     |
| D                       | -51.78                                      | 2.81                                     | 0.0618                 | 0.70           | 13.91                    | 0.60        | 5.92                     |
| E                       | -50.46                                      | 2.27                                     | 0.0683                 | 0.68           | 14.39                    | 0.51        | 5.13                     |

4. Conclusions:
In this review, the impact of acetamide on PEO and performance of gel polymer electrolyte were verified by DSSCs. The reduction of crystallinity in the GPE by the blend of acetamide due to increasing amorphous nature was examined by FTIR spectroscopy. The variation of glass transition temperature \( (T_g) \) on the GPE by the incorporation of acetamide was investigated by DSC. By the addition of acetamide, \( T_g \) decreases up to PEO/PEGDME with 10 wt% of acetamide. Ionic conductivity and temperature dependent of conductivity were investigated by BDS. The flexibility and free volume in the GPE increase with an increase of temperature and hence improve the ion mobility of the polymer systems. The ionic conductivity high for PEO/PEGDME with 10 wt% of acetamide as \( 2.81 \times 10^{-3} \) S/cm and less for the PEO without acetamide as \( 1.67 \times 10^{-3} \) S/cm. Finally, photovoltaic performance of DSSC was analyzed by the implementation of GPEs in the dye-sensitized solar cells. The GPE contains PEO/PEGDME with 10 wt% acetamide exhibits a high photovoltaic conversion efficiency of 5.92% compared with 4.35% for PEO without acetamide under 100 mW/cm\(^2\) illuminations. However, more amount of acetamide over 10 wt% decreases the photovoltaic performance of the DSSCs due to the complexation between \( I_3^- \) and acetamide which may reduce the ionic conductivity of polymer electrolyte and mobility of ions. As a result, photocurrent conversion efficiency reduces for 20 wt% of acetamide when compare to 10 wt% of acetamide.
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