

Gel Polymer Electrolyte with PEO/PEGDME added Acetamide, LiI/I₂ Composite for Dye Sensitized Solar Cell Applications

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Abstract : Gel polymer electrolytes (GPE) are intended to help ion transportation in an enormously thick medium and consume incident light more efficiently in dye-sensitized solar cells. GPEs were synthesized by the addition of acetamide in poly (ethylene oxide) (PEO) and poly (ethylene glycol) dimethyl ether (PEGDME) with LiI/I₂. PEO/PEGDME with 20 wt% acetamide provide highest efficiency ($\eta = 4.89\%$) under 100 mW cm⁻² illumination and exhibits highest ionic conductivity ($\sigma = 1.47 \times 10^{-3}$ S/cm) among the all electrolytes, compared to GPE without acetamide ($\eta = 3.04\%$). The gain in open circuit voltage (V_{oc}) for GPEs is due to the decrease in the recombination effect and electron lifetime increases by the addition of acetamide on the PEO. The short circuit current density (J_{sc}) is increased due to the growth in the ionic conductivity and amorphous nature of the GPE increases by addition of acetamide to the PEO.

Keywords: Dye sensitized solar cells (DSSC), Gel polymer electrolytes (GPE), poly (ethylene oxide) (PEO), Electrochemical Impedance Spectroscopy (EIS).

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I. Introduction

Grätzel invented dye-sensitized solar cell (DSSC) in 1991 and classified as 3rd generation solar photovoltaics. The efficiency of DSSCs reported so far is about 13% and working method is similar to the principle of plant photosynthesis [1-2]. DSSC offer an attractive alternate to conventional photovoltaic devices for conversion of solar energy to electrical energy at less manufacture cost and less environmental effect during production. Major components of DSSC are photo electrode, counter electrode and electrolyte. However, the uses of liquid electrolytes limit the long term stability of DSSCs for out-door applications owing to leakage and evaporation of volatile solvents. Significant research work has been contributed to overcome difficulties caused by liquid electrolytes and many researchers are trying to substitute the liquid electrolytes with ionic liquids, solid polymers and gel polymer electrolytes [3-8].

GPEs are the substitutes for DSSC because of the stability of the electrolytes caused due to the trapping of redox ions in the polymer matrix. De Paoli assembled DSSC by utilizing of poly (o-methoxyaniline) as sensitizer and a copolymer of poly (epichlorohydrin-co-ethylene oxide) containing NaI/I₂ based electrolyte [9]. A DSSC with PEO/P (VDF-HFP) polymer composite matrix utilizing acetamide as plasticizer along with SiO₂ nanoparticles, KI/I₂ was fabricated by Cui et al., and achieved photovoltaic conversion efficiency (PCE) of 6.04 % [10]. It is evident from the literature that efficiencies witnessed so far are sensibly low for such DSSCs made out of solid polymer electrolytes because of its low ionic conductivity in the polymer matrix and poor crystallinity. To reduce such constraints, the GPEs are utilized as a part of DSSC, which demonstrates higher ionic conductivity with excellent stability compared to both the solid and liquid electrolytes. Hence, it is focused to improve the efficiency of DSSC with GPEs [11, 12]. Usually, GPEs are set up by including a plasticizer in polymer matrix [13]. Chen et al. reported the in-situ gelation of an electrolyte including Poly (acrylonitrile-co-vinylacetate) (PAN-VA) in acetonitrile, accomplished 9.5% and 9.0% efficiencies in the presence and absence of TiO₂ nanofiller respectively [14].

In the present work, the authors demonstrated the gel polymer electrolyte (GPE) based DSSC. GPE is designed to support ion mobility in the highly viscous medium. PEO is picked as a polymer due to its polar nature with photochemical, thermal and chemical stability. An oligomer (i.e., Poly (ethylene glycol) dimethyl ether (PEGDME)) is blended to PEO to enhance the ion mobility and diffusion of electrolyte through the

mesopores of a TiO₂ based photo electrode [12,15]. Acetamide is included as a plasticizer in the polymer matrix.

II. Experimental

2.1 Materials:

Poly (ethylene oxide) (PEO, $M_w = 10^6 \text{ gmol}^{-1}$), Poly (ethylene glycol) dimethyl ether (PEGDME, $M_w = 250 \text{ gmol}^{-1}$), Acetamide, LiI, Iodide (I₂), N719 and FTO coated glass from Sigma-Aldrich, acetonitrile (Merck), Titanium dioxide (TiO₂, Dyesol), platinum solution (Solaronix) were purchased.

2.2 Preparation of Polymer Gel Electrolytes:

GPEs were prepared by adding 0.5 g of poly (ethylene oxide) (PEO) to a mixture of acetonitrile and Poly (ethylene glycol) dimethyl ether (PEGDME) under constant blending for 2 hours. To this mixture about 0.2 g of LiI, 0.08 g of I₂ and different wt% of acetamide (0%, 5%, 10%, 20%) were added and mixed for 2 more hours. The prepared electrolyte solution was kept under constant stirring during the night. Subsequently, homogeneous solution was heated at 80°C to evaporate acetonitrile and to get gel polymer electrolyte. For all GPEs, the concentration ratio was maintained at 0.4 for the iodine salt and iodide [LiI/I₂]. A series of polymer electrolytes (**A**: PEO + LiI + I₂, **B**: PEO + PEGDME + LiI + I₂, **C**: PEO + PEGDME + 5 wt% Acetamide + LiI + I₂, **D**: PEO + PEGDME + 10 wt% Acetamide + LiI + I₂, **E**: PEO + PEGDME + 20 wt% Acetamide + LiI + I₂) were prepared.

2.3 Fabrication of dye sensitized solar cell:

DSSCs were fabricated by following the procedure as mentioned below:

2.3.1 Preparation of photo electrode: Fluorine doped SnO₂ (FTO) coated glass substrates are cleaned by a soft detergent solution followed by deionized water, acetone and 2-propanol in an ultrasonic bath. A compact TiO₂ blocking layer is deposited onto the surface of cleaned FTO by treatment with 40 mM TiCl₄ solution at 70 °C for 30 min, cleaned with deionized water. Nanocrystalline titanium dioxide (TiO₂, Dyesol) transparent layer is covered onto TiCl₄ treated FTO glass substrate, repeated the process to attain 12 μm thick TiO₂ film. Further, 4 μm thick film of scatter TiO₂ (Dyesol) is coated, sintered at 500 °C for 30 min. TiCl₄ treatment is performed at 70 °C for 30 min to enhance the surface area of TiO₂. These electrodes are dipped in the N719 dye solution (0.3 mM) for 18 hr under dark condition. The obtained photo electrodes are rinsed twice by absolute ethanol to remove any unanchored dye molecules and finally dried under nitrogen purge.

2.3.2 Preparation of counter electrode: The counter electrodes are prepared by a spin coat method. Briefly, cleaned FTO substrates are placed on the substrate holder of spin coater and 40 μl of platinum solution (Solaronix) is dispensed and rotated of 5000 RPM for 30 sec, followed by sintering at 500 °C for 15 min.

2.3.3 DSSC Assembling: Test cells are fabricated by use of 60μm thickness polymer film, which is placed between the counter electrodes and photo electrodes, and the developed polymer gel electrolytes are filled in between. The fabricated DSSC has an active area of 0.16 cm².

2.4 Characterizations:

The structural properties of GPE are studied by Philips: PW1830 X-ray diffractometer. Fourier transform infrared spectra (FTIR) of the GPEs are measured by BRUKER FT-IR Spectrometer. Surface morphology is obtained by Hitachi Model S-3400N SEM instrument. DSC thermograms are studied at the heating rate of 10°C min⁻¹ with help of a Mettler-Toledo DSC1 instrument. The conductivity of the GPEs is studied by electrochemical impedance spectroscopy (EIS). Current density-Voltage (J-V) characteristics are done with the PEC-L01 solar simulator (Pacell Inc.) connected to source meter (2401, Keithley). The simulator is calibrated with standard Si cell to get 100 mW/cm² output power (1 Sun condition). Electrochemical impedance spectroscopy (EIS) studies are conducted by use of IVIUMSTAT (IVIUM) with amplitude of 10 mV, frequency range of 0.1 Hz to 1 MHz under 1 Sun condition.

III. Results and discussion

3.1 Fourier transforms infrared spectroscopy:

FTIR is helpful to understand the structural, crystalline modifications and complexation in the GPEs. FTIR spectra of the GPEs are shown in Fig 1. The stretching vibrations of -CH₂ in PEO occurs at 2871 cm⁻¹ due

to the interaction of Lithium ion and acetamide with polymer in GPE and intensity of this peak decreases. These changes of $-CH_2$ confirms the coordination between PEO and acetamide. Further, a characteristic peak observed due to C-O-C stretching vibrations at 1110 cm^{-1} in PEO chain [16]. For GPEs containing acetamide this peak gets sharpened and the intensity also reduced upon addition of acetamide content up to 20 wt%. At the same time, the peak observed at 1340 cm^{-1} due to the characteristic of the crystallized PEO gets to decrease upon addition of acetamide content up to 20 wt%. The absorption peaks of acetamide are observed due to the presence of $-NH_2$ and $-C=O$ groups at 1659 cm^{-1} and 3460 cm^{-1} respectively.

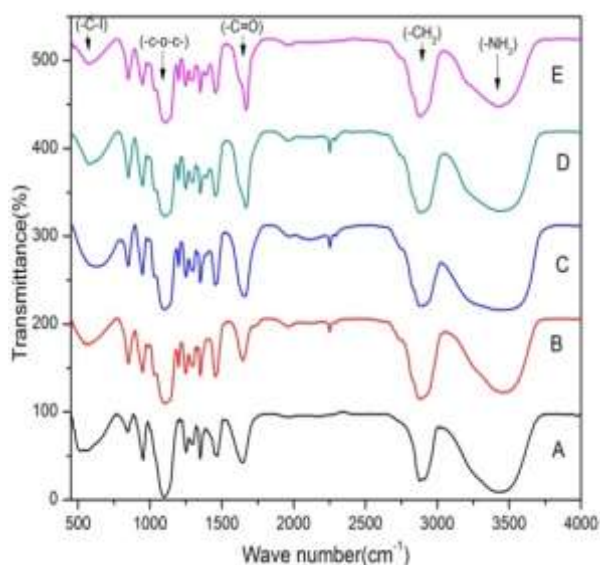


Figure1: FTIR spectra of GPEs (A, B, C, D and E indicates PEO with different wt% of acetamide).

3.2 Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) is done to analyze the phase modulation of the gel polymer electrolytes. The DSC thermogram shown in Fig.2 contains a different wt % of acetamide in GPE. The flexibility of the polymer can be explained by one of the important parameter know as glass transition temperature (T_g). The temperature at which the material undergoes changes from crystalline, brittle state to elastic state is called the glass transition temperature (T_g). The T_g values of the acetamide modified GPE and without acetamide GPE are given in the Table-1. By addition of acetamide, T_g decreases up to PEO/PEGDME 20 wt% of acetamide. This shows that the increase in the amorphous nature and also increase free volume of the GPE by addition of acetamide, as a result mobility of the ions is improved which indicates that the ionic conductivity of GPEs also increases[17,18].

3.3 Structural properties:

The X-ray diffraction studies provide to study the 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 Fig. 3. Pure PEO is a semi crystalline polymer and exhibits two strong crystalline peaks at 19.1° and 23.2° [19]. The XRD pattern shows only one broad peak, which indicates the variation in the crystalline phase of gel polymer electrolytes. The diffraction peaks become broad when acetamide content is inserted in the polymer complexes. Hence, it can suggest that the polymer undergoes significant structural reorganization 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 [20]. Among all GPEs, acetamide content with 20 wt% shows broad and less intensity curve, which exhibits high amorphous nature compare to others and is confirmed by FTIR, DSC.

3.4 Scanning electron microscopy:

SEM image of GPEs with various wt% of acetamide are presented on the Fig.4. Scanning electron micrographs revealed that the redox couple bound inside the walls of the gel structure establishes a homogeneous allotment. SEM images show small spherical particles accumulated by addition of acetamide. Thus, incorporation of acetamide provides significant modifications in the morphology and increase in the free volume of the GPE growth in the ionic conductivity.

3.5. Ionic conductivity of gel polymer electrolytes:

In DSSC, the power conversion efficiency depends upon the transportation of the redox couple and ionic conductivity of the gel polymer electrolyte [21]. Fig. 5 shows the Nyquist plots of fabricated DSSCs for gel polymer electrolytes by electrochemical impedance spectroscopy (EIS). Therefore, the ionic conductivity of the prepared GPEs is measured by bulk resistance (R_b) values obtained in electrochemical impedance spectroscopy (EIS) by applying the formula:

$$\sigma = \frac{l}{AR_b}$$

Where ' l ' is the space between two electrodes, ' A ' is the area and ' R_b ' is the bulk resistance measured from EIS spectrum. From Table-1, it is resolved that the ionic conductivity of GPE is maximum for 20 wt% acetamide. It is observed that ionic conductivity is large in the amorphous phase of GPE [22]. Ionic conductivity increased by addition of acetamide; this is due to the decrease of crystallinity of the GPE and due to the interaction of acetamide with PEO. The above information is in better agreement with the resolutions provided in FTIR and DSC measurements.

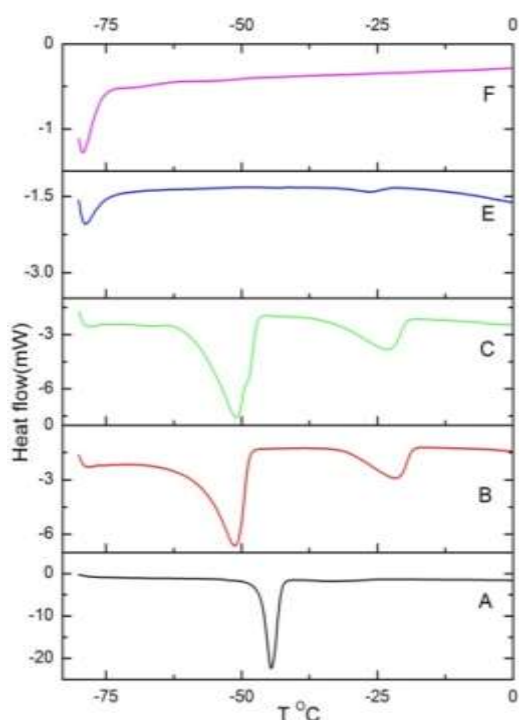


Figure 2: DSC thermograms of GPEs (A, B, C, D and E indicates PEO with different wt% of acetamide) .

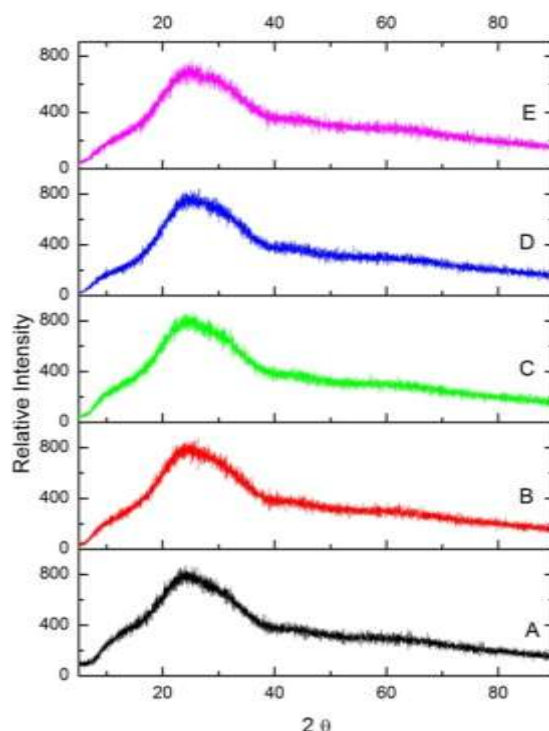
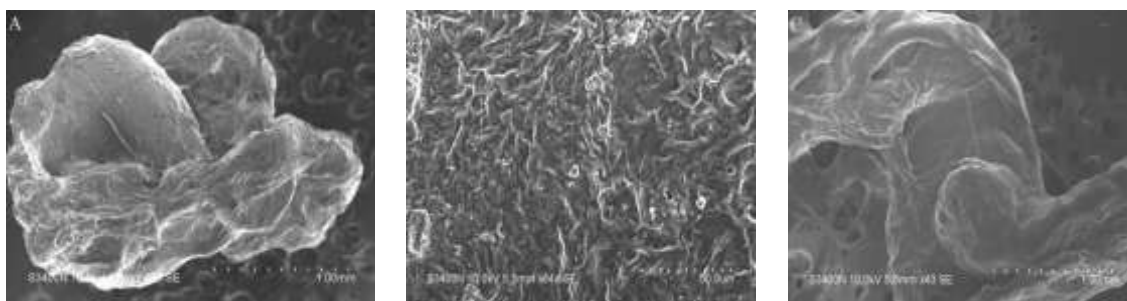


Figure 3: X-ray diffraction pattern of GPEs (A, B, C, D and E indicates PEO with different wt% of acetamide).



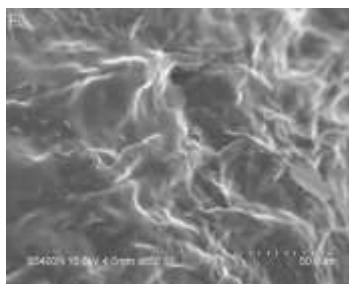
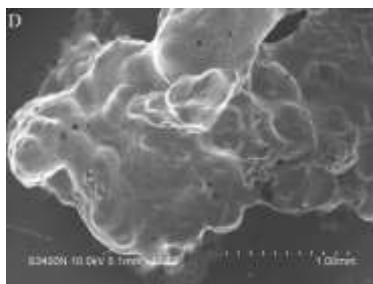


Figure 4: SEM images of GPEs (A, B, C, D and E indicates PEO with different wt% of acetamide).

Table.1: Gel polymer electrolyte parameters and Photovoltaic cell parameters of fabricated test cells.

Parameter	A	B	C	D	E
Glass transition temperature T_g °C	-44.57	-51.13	-51.28	-78.86	-79.18
Conductivity σ mS/cm	1.194	1.329	1.254	1.364	1.47
V_{oc} (V)	0.63	0.60	0.62	0.63	0.76
J_{sc} (mA/cm ²)	8.39	7.89	12.47	13.56	11.71
Fill Factor	0.58	0.37	0.46	0.50	0.55
Efficiency η (%)	3.04	1.76	3.54	4.30	4.89

3.6 Current density – Voltage (J-V) characteristics:

DSSCs are fabricated to determine the performance of prepared gel polymer electrolyte potentiality in a practical application. Fig. 6 reveals the current density-voltage (J-V) characteristics of DSSCs using platinum electrodes under simulated solar irradiation of 100 mW/cm² (AM 1.5). The power conversion efficiency of Cell-E shows higher performance of $\eta = 4.89\%$, $J_{sc} = 11.71$ mAcm⁻², $V_{oc} = 0.76$ V and $FF = 0.55$, which indicates that the GPE-E is having good potentiality than the other electrolytes. A systematic study is conducted to assess the acetamide and PEGDME loads in gel electrolytes as shown in Fig. 6. The conversion efficiencies of DSSCs with different lithium concentrations are 3.40 %, 1.76 %, 3.54 %, 4.30 % and 4.89 % for Cell-A, Cell-B, Cell-C, Cell-D and Cell-E respectively and the other photovoltaic parameters evaluated from the J-V characteristic are given in Table-1.

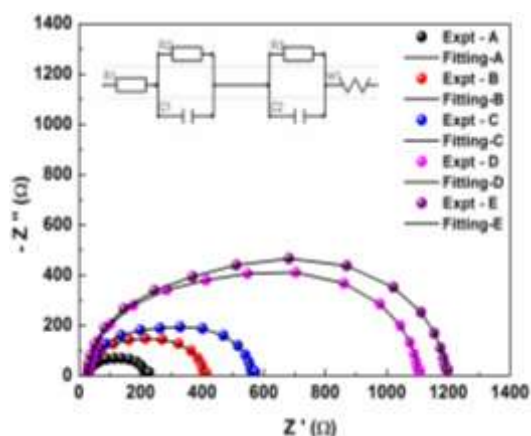


Figure 5: Nyquist plots of fabricated DSSCs with gel polymer electrolytes.

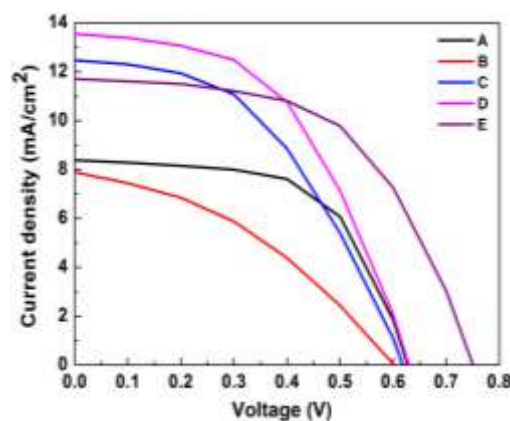


Figure 6: Current density - Voltage characteristics of DSSCs under 1 sun illumination.

IV. Conclusions

In this study, the effect of acetamide in PEO gel polymer electrolyte on the performance of DSSCs was verified. The decrement of crystallinity on the GPE by the addition of acetamide was studied by FTIR spectroscopy and the variation of glass transition temperature (T_g) on the GPE by the incorporation of acetamide was investigated by DSC. Ionic Conductivity was investigated by electrochemical impedance spectroscopy. The ionic conductivity for the GPE without acetamide was found to be 1.194×10^{-3} S cm⁻¹ and is high for 20 wt% of acetamide which was 1.47×10^{-3} S cm⁻¹. Finally, photovoltaic performance of DSSC was analyzed by introducing GPEs in the dye-sensitized solar cells. The gel polymer electrolyte with 20 wt% acetamide exhibited a high photovoltaic conversion efficiency of 4.89% compared with 3.04% for GPE without acetamide under 100

mW cm⁻² illuminations. This is due to the increase in the amorphous nature of the polymer matrix and increase in the ions mobility in the polymer system.

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