

Studies of solvent effect on the conductivity of 2-mercaptopyridine-doped solid polymer blend electrolytes and its application in dye-sensitized solar cells

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ABSTRACT: Solvents and electrolytes play an important role in the fabrication of dye-sensitized solar cells (DSSCs). We have studied the poly(ethylene oxide)-poly(methyl methacrylate)-KI-I₂ (PEO-PMMA-KI-I₂) polymer blend electrolytes prepared with different wt % of the 2-mercaptopyridine by solution casting method. The polymer electrolyte films were characterized by the FTIR, X-ray diffraction, electrochemical impedance and dielectric studies. FTIR spectra revealed complex formation between the PEO-PMMA-KI-I₂ and 2-mercaptopyridine. Ionic conductivity data revealed that 30% 2-mercaptopyridine-doped PEO-PMMA-KI-I₂ electrolyte can show higher conductivity ($1.55 \times 10^{-5} \text{ S cm}^{-1}$) than the other compositions (20, 40, and 50%). The effect of solvent on the conductivity and dielectric of solid polymer electrolytes was studied for the best composition (30% 2-mercaptopyridine-doped PEO-PMMA-KI-I₂) electrolyte using various organic solvents such as acetonitrile, *N,N*-dimethylformamide, 2-butanone, chlorobenzene, dimethylsulfoxide, and isopropanol. We found that ac-conductivity and dielectric constant are higher for the polymer electrolytes processed from *N,N*-dimethylformamide. This observation revealed that the conductivity of the solid polymer electrolytes is dependent on the solvent used for processing and the dielectric constant of the film. The photo-conversion efficiency of dye-sensitized solar cells fabricated using the optimized polymer electrolytes was 3.0% under an illumination of 100 mW cm^{-2} . The study suggests that *N,N*-dimethylformamide is a good solvent for the polymer electrolyte processing due to higher ac-conductivity beneficial for the electrochemical device applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42489.

KEYWORDS: applications; blends; conducting polymers; plasticizer; polymer electrolytes

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INTRODUCTION

Polymer electrolytes received great attention during the last few decades due to their potential applications in electrochemical devices such as rechargeable lithium ion batteries, photoelectrochemical solar cells, electrochromic display windows, and sensors.¹⁻⁴ The polymer electrolytes have several advantages over liquid electrolytes such as good adherence to the electrode, flexible geometry, low volatility, and high energy density.^{5,6} The polymer electrolytes with iodide/triiodide (I^-/I_3^-) redox couple are most investigated solid state electrolytes because of its conducting properties, simple preparation, and low production cost. The polymers generally used for the electrolytes developments are polyethylene oxide (PEO), polyvinylpyrrolidone (PVP), poly(methyl methacrylate) (PMMA), polyvinylidene fluoride (PVDF), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), and polyvinyl alcohol (PVA).^{5,7-9} Among the polymer, PEO is having

the highest ability to solvate the inorganic salts undergo easy complexation and possess low glass transition temperature (T_g), etc.¹⁰ However, the ionic conductivity of PEO-based polymer electrolyte was very poor. Beside other properties of polymer electrolytes the ionic conductivity is a crucial requirement in the applications of electrochemical devices. The ionic conductivity of polymer electrolytes has been improved either by reducing the crystalline nature of the polymer or by lowering the T_g .¹¹ The various approaches have been adapted to increase the ionic conductivity of polymer electrolytes viz. blending of polymer with another polymer, incorporation of inert fillers, and plasticization.¹²⁻¹⁴ The most successful approach to improving the ionic conductivity is the incorporation of substantial amounts of organic plasticizer into the polymer electrolytes such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), and organic nitrogenous compounds.¹⁵⁻¹⁷ The addition of plasticizer to

polymer electrolytes reduces the crystalline content, glass transition temperature and increasing the polymer segmental mobility. Thereby, the ions can easily migrate in the free volume of polymer electrolytes which leads to the enhancements of the ionic conductivity of polymer electrolytes. Another promising useful method is blending of individual polymer with other polymer to develop new materials with improved mechanical stability.

In this study, PEO was blended with PMMA to form a new polymer matrix. The miscibility of components is very important for choosing of polymer blends. It is clear from the reported literatures that PEO is miscible in PMMA.^{11,18} PEO is chosen as the electrolyte medium because of its polar and chemically stable nature. The repeating (-CH₂-CH₂-O-) group in the structure of PEO makes the favorable arrangement for the effective interaction between the alkali metal cations and ether oxygen. Thus, the weak coulombic interaction facilitates the integration of ion with the polymer and reduced the PEO crystallinity. The reduced crystalline phase favors the hoping inter- and intra- chain ion movements.¹⁹ The presence of the ester functional group in PMMA makes it as a suitable polymer for the preparation of blending via the carbonyl oxygen atoms (C=O) as an electron donor.²⁰ 2-mercaptopyridine has been chosen as a plasticizer because it contains both nitrogen (N) as well as sulfur (S) linkage in its structure that is expected to improve the performance of polymer electrolytes by forming a charge transfer complex through its lone pair of electrons. Muthuraaman *et al.*, reported that the 2-mercaptopyridine-doped PEO-KI-I₂ electrolytes enhanced the solar energy conversion efficiency.²¹

In this study, the PEO-PMMA-KI-I₂ polymer blend electrolytes with different amounts of 2-mercaptopyridine were prepared and the best conducting composition was optimized based on AC impedance analysis. Further, the effect of solvent on the conductivity of polymer electrolytes was studied using various organic solvents for the optimized solid polymer electrolytes and finally the device performances of polymer electrolytes in dye-sensitized solar cell was evaluated.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO, $M_w \sim 5,000,000$), Poly(methyl methacrylate) (PMMA, $M_w \sim 3,50,000$) and 2-Mercaptopyridine were obtained from Sigma Aldrich. Potassium iodide (KI) and iodine (I₂) were purchased from Nice chemicals, India. Platinum catalyst solution (Plastisol) and Ruthenium (N719) dye were purchased from Solaronix, Switzerland. All organic solvents *N,N*-dimethylformamide, acetonitrile, chlorobenzene, dimethylsulfoxide, 2-butanone, and isopropanol used in the experiments were purchased from SDFCL, India. TiO₂ nanoparticles (P25 and P90) were provided by Degussa, Germany. All reagents were used without further purification.

Preparation of Polymer Blend Electrolyte Film

Polymer blend electrolyte films were prepared by the solution cast technique. An amount of 0.24 g of PEO, 0.06 g of PMMA, 0.03 g of KI, 0.006 g of I₂ and various weight percentage ratios of 2-mercaptopyridine (2-MCP) (0, 20, 30, 40, and 50%) with

respect to KI were dissolved in 25 mL of acetonitrile and magnetically stirred with heating for about 3 h at 60°C. Then, this polymer solution was poured in a Teflon petri dish and dried in vacuum oven for 12 h for solvent evaporation.

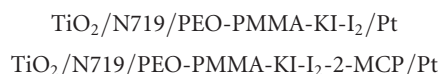
Similarly the polymer blend films in other organic solvents were also prepared but the heating temperature was maintained differently depending on the boiling point of the solvent used.

Characterization of Polymer Electrolyte Films

The prepared blended polymer electrolyte films were characterized by Fourier transform infrared (FTIR) spectroscopy (Shimadzu IR Affinity-1 FTIR spectrometer) and the spectra were recorded in the wave number range from 4000 to 400 cm⁻¹. The X-ray diffraction (XRD) patterns were recorded using a Siefert model SF 60 XRD system with Cu K_α radiation ($\lambda = 0.154$ nm) at a scan speed of 3°/min. Electrochemical impedance spectroscopy (EIS) measurement of the polymer electrolytes was carried out using the electrochemical workstation (CHI model 608E) over the frequency range from 20 Hz to 1 MHz with a symmetrical cell set-up Stainless steel (SS) disc/electrolyte film/SS disc for mounting the electrolyte samples. Frequency dependence of dielectric measurements was measured using HIOKI 3532-50 LCR Hi TESTER at room temperature (303 K).

Fabrication of Dye-Sensitized Solar Cells (DSSCs)

The TiO₂ photoelectrode was prepared by nanocrystalline TiO₂ particles coated on the fluorine-doped tin oxide (FTO) conducting glasses in two layers. In order to form a thin TiO₂ compact layer, TiO₂ (P90) paste was spin coated at 2650 rpm for 60 s on the conducting surface of FTO and followed by sintering at 450°C for 30 min. The compact layer is to improve the adhesion of TiO₂ to the substrate and also preventing back electron flow from conducting surface of FTO into redox electrolytes in the solar cells.^{22,23} The second layer of TiO₂ (P25) paste was doctor-bladed on the compact layer and again sintering at 450°C for 30 min to obtain TiO₂ photoelectrode. The dye was sensitized on the TiO₂ photoanode by immersing in 0.3 mM ethanol solution of N719 dye [Cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium)] for 24 h at room temperature. The platinum counter electrode was prepared by drop casting of plastisol solution on the FTO conducting surface and sintered at 450°C for 30 min. The assembly of DSSC was fabricated using the prepared polymer electrolytes sandwiched in between the TiO₂ photoanode and Pt-counter electrode. The polymer electrolyte was spread evenly on the surface of dye-sensitized TiO₂ photoanode. Finally, the two electrodes are overlaid and held together with clamps without any sealing. The active area of DSSC was 0.196 cm² and all photovoltaic measurements were performed in the open air. The cell configurations are prepared in this study are



The photocurrent-voltage ($J-V$) characteristics of the fabricated DSSCs were measured under illumination of simulated intensity

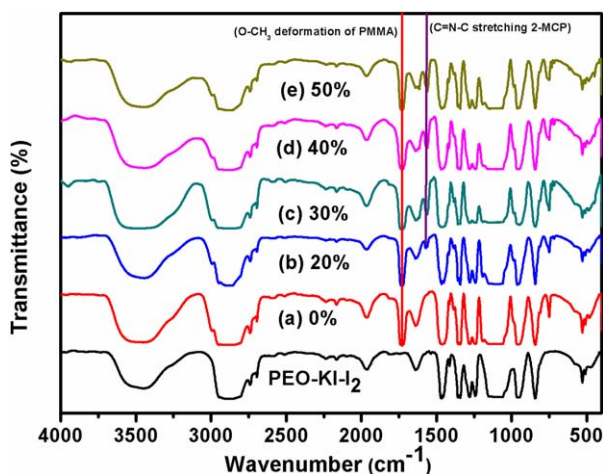


Figure 1. FTIR spectrum of PEO-KI-I₂ and different wt % of 2-MCP (a) 0%, (b) 20%, (c) 30%, (d) 40%, and (e) 50% doped PEO-PMMA-KI-I₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 100 mW/cm². The fill factor (FF) and overall power conversion efficiency were calculated using the following equations

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta(\%) = \frac{V_{\max} \times J_{\max}}{P_{in}} \times 100 = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100 \quad (2)$$

where, V_{oc} is the open circuit voltage (mV), J_{sc} is the short circuit current density (mA/cm²), P_{in} is the incident light power and J_{\max} (mA/cm²), and V_{\max} (mV) are the current density and voltage in the J - V curve respectively at the point of maximum power output.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectral Studies

The Fourier transform infrared (FTIR) spectra obtained for the polymer electrolytes such as PEO-KI-I₂, PEO-PMMA-KI-I₂ and 2-MCP-doped PEO-PMMA-KI-I₂ polymer blend electrolytes are shown in Figure 1. The major frequencies (cm⁻¹) and assignment for the PEO-KI-I₂, PEO-PMMA-KI-I₂, and PEO-PMMA-

KI-I₂-2-MCP polymer electrolytes have been summarized in Table I. The characteristic absorption peaks of PEO at 2854 cm⁻¹ and 1094 cm⁻¹ are corresponds to the -CH₂ linkage and C-O-C stretching vibration, respectively.²⁴ The absorption bands at 1359 cm⁻¹ and 1242 cm⁻¹ are attributed to the -CH₂ wagging and a couple of CH₂ twisting modes. The pair of absorption peaks appearing at 962 cm⁻¹ and 842 cm⁻¹ may be assigned to the CH₂ rocking configuration.²⁵ In the FTIR spectrum of PEO-PMMA polymer blend electrolytes, the absorption peaks at 1730 cm⁻¹ are assigned to O-CH₃ deformation of PMMA. It can be observed that a new peak at 750 cm⁻¹ may be due to the interaction between the oxygen atom of PEO and carbonyl carbon atoms of PMMA.¹¹ In the FTIR spectrum of PEO-PMMA-KI-I₂/2-MCP, the peak at 1562 cm⁻¹ correspond to the stretching frequency of -C=N-C group of 2-MCP and it is clear that the intensity of peak is increased with increase in the amount of 2-MCP. Therefore, the FTIR results clearly prove the complexation of 2-MCP with PEO-PMMA-KI-I₂ polymer electrolytes. The molecular structure of the polymers and PEO-PMMA-KI-I₂-2-MCP electrolyte are shown in Figure 2.

X-ray Diffraction Analysis

The X-ray diffraction patterns obtained for pure PEO-KI-I₂, PEO-PMMA-KI-I₂ and different wt % ratios of 2-MCP-doped PEO-PMMA-KI-I₂ polymer electrolyte systems are shown in Figure 3. The diffraction peaks of PEO are observed at $2\theta = 18.6^\circ$ and 23.1° .²⁶ It can be seen that the intensity of PEO peaks is decreased and hence its crystallinity also decreased when PMMA is blended with PEO. Further, the addition of 2-MCP in PEO-PMMA leads to the formation of the same peaks but of low intensity. Thus, the conversion of crystalline into amorphous nature on blending enables the free flow of ions and hence the overall conductivity of the electrolytes has been improved.²¹ The XRD spectrum clearly shows that the intensity of 30% ratio of 2-MCP-doped polymer blend electrolytes is very low. The present XRD results can be inferred as, 30 wt % of 2-MCP interacted well with the polymer electrolyte and exhibited more amorphous nature than the other electrolytes. This increase in amorphous nature may help to enhance the diffusivity of ions which in turn favors to attain high ionic

Table I. The Frequencies (cm⁻¹) and Assignments for the PEO-KI-I₂, PEO-PMMA-KI-I₂, and PEO-PMMA-KI-I₂-2-MCP

PEO-KI-I ₂ (wavenumber cm ⁻¹)	PEO-PMMA-KI-I ₂ (wavenumber cm ⁻¹)	PEO-PMMA-KI-I ₂ -2-MCP (wavenumber cm ⁻¹)	Assignments
2854	2854	2854	-CH ₂ stretching of PEO
1094	1094	1094	C-O-C stretching PEO
1359	1359	1359	-CH ₂ wagging
1242	1242	1242	-CH ₂ twisting
962	962	962	-CH ₂ rocking
842	842	842	-CH ₂ rocking
-	1730	1730	O-CH ₃ deformation of PMMA
-	450	450	Interaction between O atom of PEO and carbonyl carbon atom of PMMA
-	-	1562	C=N-C stretching of 2-MCP

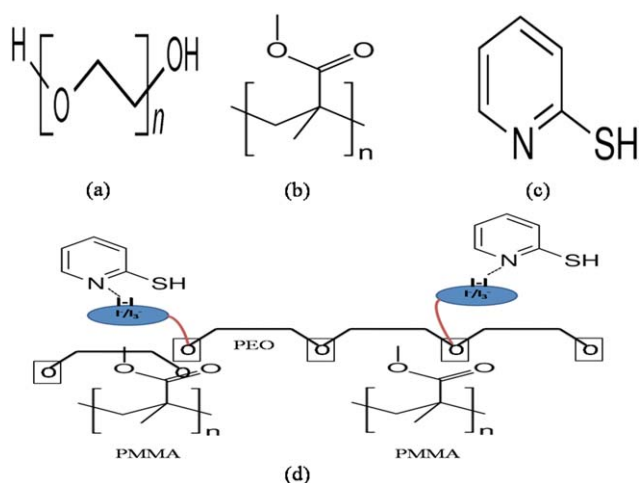


Figure 2. The molecular structures of (a) PEO, (b) PMMA, (c) 2-MCP, and (d) PEO-PMMA-KI-I₂-2-MCP electrolyte. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity and thus will serve as an efficient electrolyte for the electrochemical devices.

Electrochemical Conductivity Studies

The ionic conductivities obtained for the polymer blend electrolytes with different weight ratios of 2-MCP at room temperature (303 K) are shown in Figure 4(a). The zoomed view of lower part of the Nyquist impedance spectra is shown in Figure 4(b). The ionic conductivity (σ) of the polymer electrolyte is calculated by the following equation.

$$\sigma = t/(R_b A) \quad (3)$$

where, t is the thickness of the film, R_b is the bulk resistance of the electrolyte obtained from the intercept on the real axis at the high frequency end of the Nyquist plot and A is the most common area covered by the electrodes in contact with the sample.²⁷ The ionic conductivity of PEO-KI-I₂ and PMMA blended PEO-KI-I₂ are calculated using Nyquist plot and it was found to be $3.95 \times 10^{-6} \text{ S cm}^{-1}$ and $4.18 \times 10^{-6} \text{ S cm}^{-1}$, respectively. The increase in ionic conductivity by blending could be due to the reduction of crystalline nature of the polymer electrolytes. The ionic conductivities of the synthesized polymer electrolytes measured at 303 K for different amounts (20, 30, 40, and 50%) of 2-MCP are shown in Table II. It can be seen that the ionic conductivity initially increased with a small addition of 2-MCP say 20 and 30%. While beyond the 30% ratio of plasticizer, the conductivity is decreased. A high ionic conductivity of $1.55 \times 10^{-5} \text{ S cm}^{-1}$ is observed for 30% of plasticizer addition. In general, the ionic conductivity of the polymer electrolyte depends on the concentration of the conducting species and their mobility. The 2-MCP added to the redox couple form a charge-transfer complex with iodine thereby reducing the sublimation of iodine and enhancing the conductivity of polymer electrolytes.²⁸ The decrease of conductivity after 30% weight ratios may be due to the torturing of the ion conduction paths by taking up some free volume, thereby decreasing the mobility of the charge carriers.^{29,30}

Dielectric Measurements

The dielectric measurements of the polymer electrolytes can be used to show importance of charge carriers or free mobile ions in the conduction behavior of the polymer electrolytes. If the dielectric property of the material increases the amount of charge stored by the material will also increase.³¹ The dielectric properties of the materials are characterized by the complex permittivity (ϵ).³²

$$\epsilon = \epsilon' - j \epsilon'' \quad (4)$$

where ϵ' is the real relative part of the complex permittivity and also referred as the dielectric constant, ϵ'' is the imaginary part of the complex permittivity and referred to dielectric loss and $j = \sqrt{-1}$. The frequency (f) dependence of the dielectric constant (ϵ') and dielectric loss (ϵ'') for the polymer electrolyte films prepared at different organic solvents are shown in Figure 5(a,b), respectively. The dielectric constant or relative permittivity is determined using the following equation.

$$\epsilon_r(\epsilon') = C_p \times t / \epsilon_0 \cdot A \quad (5)$$

where, C_p is the capacitance of the sample, t is the thickness of the polymer film, A is the area of the sample. ϵ_0 is the dielectric permittivity of a vacuum ($8.854 \times 10^{-12} \text{ F/M}$). The dielectric loss or loss tangent plotted using $\tan \delta$.

In all cases dielectric constant (ϵ') and dielectric loss (ϵ'') values are increasing with a decrease in applied frequency. It may be attributed to the electrical relaxation processes and the insufficient time for dipoles to align before the field changes its direction. At the high frequency range, the dipoles are unable to orient themselves in the direction of the applied field and hence the value of the dielectric constant decreases.³³ Dielectric property provided valuable information such as characteristic of the ionic/molecular interaction of the polymer electrolyte and the ion transport behavior. The increase in dielectric constant implies the increase in the number of ions.³⁴ In this study, dielectric constant (ϵ') and dielectric loss (ϵ'') values are high for the DMF solvent used polymer electrolyte film than the

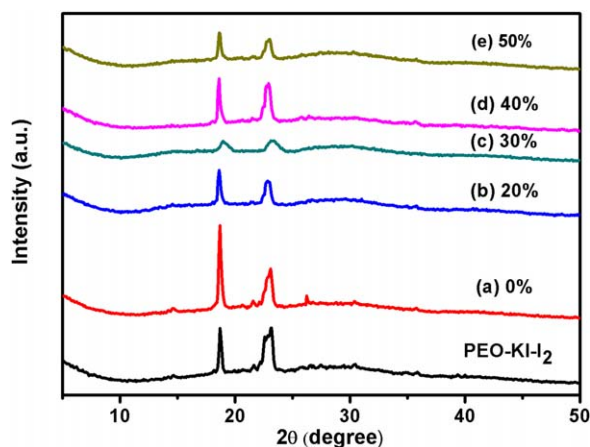


Figure 3. The X-ray diffraction patterns of PEO-KI-I₂ and different wt % ratios of 2-MCP (a) 0%, (b) 20%, (c) 30%, (d) 40%, and (e) 50% doped PEO-PMMA-KI-I₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

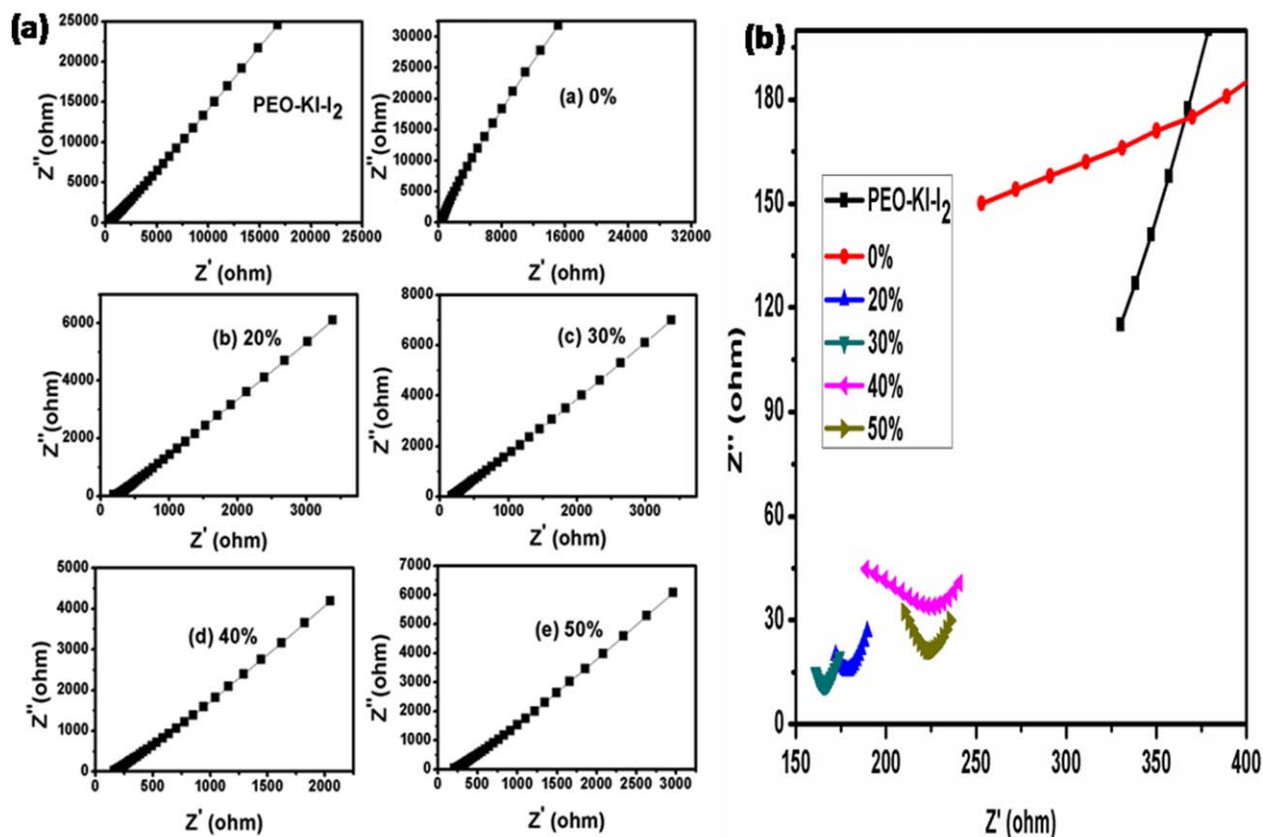


Figure 4. (a) Nyquist impedance spectra of PEO-KI-I₂ and different wt % ratios of 2-MCP (a) 0%, (b) 20%, (c) 30%, (d) 40%, and (e) 50% doped PEO-PMMA-KI-I₂ at room temperature (303 K), and (b) The zoomed view of lower part of Nyquist impedance spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other solvents. Hence, DMF is expected to show the highest conductivity values than other solvents.

Electrical A.C Conductivity (σ_{ac}) Studies

The effect of dielectric constant on the conductivity behavior was investigated for the optimized 30% 2-MCP-doped polymer electrolyte film prepared by using various organic solvents. The variation of σ_{ac} with frequency for the electrolyte film is shown in Figure 6. The ac conductivity of polymer electrolytes is calculated using the following equation using the dielectric measurement data.³²

Table II. The Ionic Conductivities of the PEO-PMMA-KI-I₂ Polymer Electrolytes Measured at 303 K for Different Amounts (0, 20, 30, 40, and 50%) of 2-MCP

System	Weight ratio of 2-MCP (%)	Ionic conductivity (S cm ⁻¹)
PEO-KI-I ₂	–	3.95×10^{-6}
a	0	4.18×10^{-6}
b	20	1.20×10^{-5}
c	30	1.55×10^{-5}
d	40	1.17×10^{-5}
e	50	8.52×10^{-6}

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta \quad (6)$$

where f is the frequency of the applied field, ϵ_0 is the dielectric permittivity of vacuum ($\epsilon_0 = 8.854 \times 10^{-12}$ F/M), ϵ_r is the relative permittivity of the polymer electrolyte and $\tan \delta$ is the loss tangent obtained from the dielectric measurements. The observed low frequency dispersive region describes the electrode-electrolyte interfacial phenomena and it may be attributed to the space charge polarization at the blocking electrode. In the low frequency region, the conductivity decreases because as frequency decreases more charge accumulation occurs at the electrode-electrolyte interface which leads to decrease in number of mobile ions. In the high frequency dispersive region, the ionic conductivity increases with increasing frequency due to the higher mobility of charge carriers, which is associated with ac conductivity of the polymer electrolytes.^{35,36}

Polymer blend electrolytes prepared by using DMF showed the higher ac conductivity. DMF denotes the oxygen having coordination bond for complexation of solvent and salt. Still, it is complicated to understand the effect of solvent on solid polymer electrolytes because the polymer electrolyte film was dried to solvent free. It can be understood from this study that the conductivity of the film is strongly dependent on the dielectric constant of the film. The high dielectric constant may lead to more dissociation of inorganic salts as a result increases the conductivity.

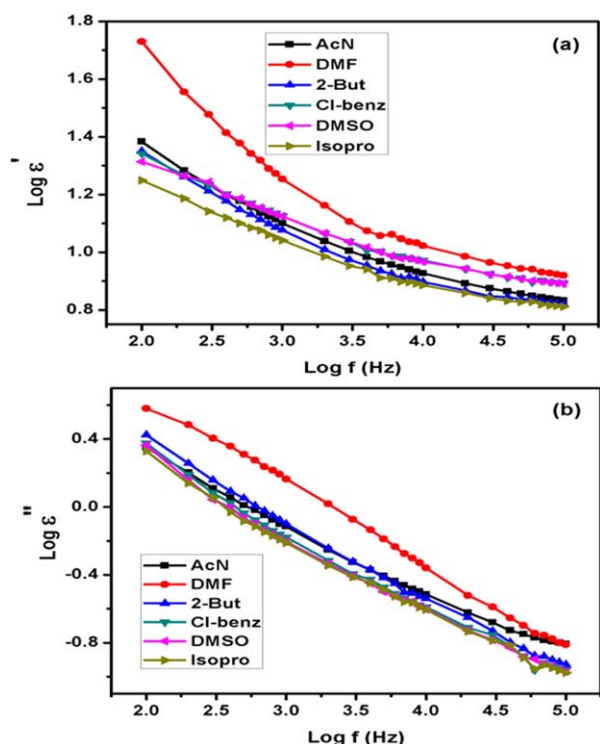


Figure 5. (a) The frequency dependence of the dielectric constant and (b) dielectric loss of 30% 2-MCP-doped PEO-PMMA-KI-I₂ films prepared at different organic solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Current-Voltage Characteristics of the DSSCs

The photocurrent-voltage (J - V) curves of the DSSCs fabricated with PEO-PMMA blend and 30% 2-MCP-doped PEO-PMMA-KI-I₂ polymer electrolytes are shown in Figure 7. The open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF) and the efficiency obtained from J - V curves are summarized in

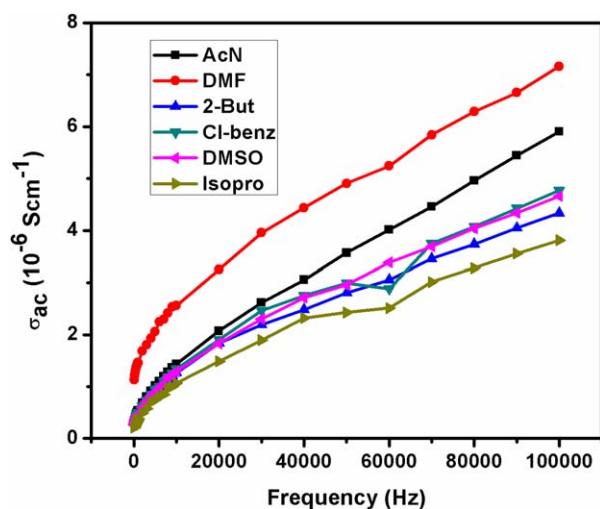


Figure 6. The variation of σ_{ac} with frequency for the electrolyte film prepared by using various organic solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

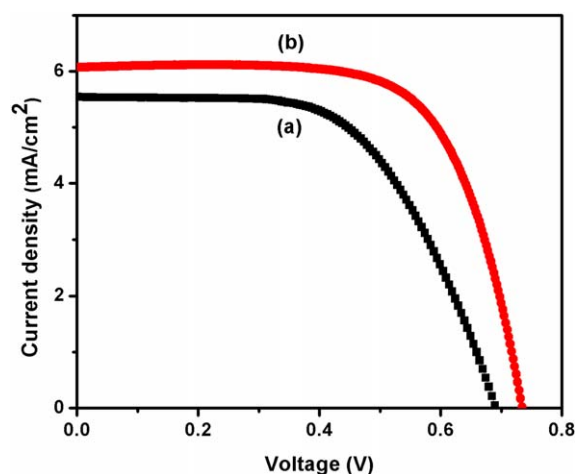


Figure 7. The photocurrent-voltage (J - V) curves of the DSSCs fabricated with (a) PEO-PMMA-KI-I₂ blend and (b) 30% 2-MCP-doped PEO-PMMA-KI-I₂ polymer electrolytes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. It can be seen that the 2-MCP-doped PEO-PMMA blend DSSCs exhibits better performance than the undoped PEO-PMMA blend electrolytes. The DSSCs with 2-MCP-doped PEO-PMMA-KI-I₂ electrolytes showed the best performance with V_{oc} of 0.73 V, J_{sc} of 6.06 mA/cm², FF of 0.69 and overall conversion efficiency of 3.0%. The enhancement of DSSC efficiency with 2-MCP-doped PEO-PMMA-KI-I₂ electrolytes may be due to high π -electron density of 2-MCP makes the better formation of charge transfer complex with iodine in redox couple.^{21,37} In our previous report,³⁸ we have investigated the influence of 2-MCP in polyvinylidene fluoride/KI/I₂ polymer electrolyte for the DSSC and optimized that the 30% 2-MCP-doped PVDF/KI/I₂ showed the highest power conversion efficiency of 2.65%, which was higher than the efficiency of DSSC fabricated using undoped PVDF/KI/I₂ polymer electrolytes (1.18%). Also, similar observation was noted in the present study, we prepared PEO-PMMA-KI-I₂ polymer blend electrolytes and fabricated the DSSC using 30% 2-MCP-doped PEO-PMMA-KI-I₂ electrolytes. The power conversion efficiency of DSSC with 30% PEO-PMMA-KI-I₂ was found to be 3.0%, whereas DSSC fabricated with undoped PEO-PMMA-KI-I₂ polymer electrolytes showed only 2.2% at the optimized conditions.

The schematic cell configurations of the DSSCs fabricated using polymer electrolytes is shown in Figure 8. It is known that the circuit is completed with an efficient transport of iodide and triiodide in the electrolytes³⁹ and the electron migration is given by the following equations 7–9.

Table III. The Current-Voltage (J - V) Curve Data of Systems (a) PEO-PMMA-KI-I₂ and (b) 30 wt % 2-MCP-Doped PEO-PMMA-KI-I₂ of DSSC under the Illumination of 100 mW/cm²

System	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	Efficiency, η (%)
(a)	0.69	5.54	0.59	2.2
(b)	0.73	6.06	0.69	3.0

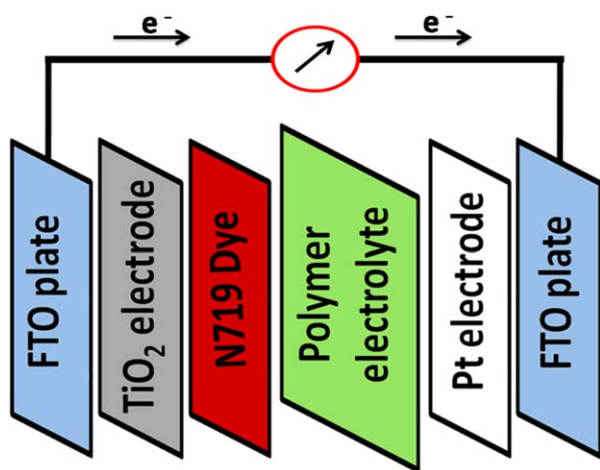


Figure 8. The schematic cell configurations of the DSSCs fabricated using polymer electrolytes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



The introduction of 2-MCP increases the concentration of I^- and decreases the I_3^- ion concentration. Therefore, the sublimation of the I_2 is reduced and the stability of DSSC also increased. It is clear from the above characteristic studies that the 30% 2-MCP-doped PEO-PMMA-KI- I_2 electrolytes prepared by using DMF solvent based electrochemical devices shows the best performance due to its reduced crystalline nature and high ionic conductivity.

CONCLUSIONS

The polymer blends PEO-PMMA-KI- I_2 with different wt % ratios of 2-MCP-doped electrolyte films were prepared by solution casting technique. The prepared films were characterized by FTIR, XRD, and A.C impedance analysis. The complex formation and amorphous nature of the polymer electrolytes were confirmed by FTIR and XRD techniques. The ionic conductivity of the polymer electrolyte film was studied using A.C impedance technique. The higher ionic conductivity value of $1.55 \times 10^{-5} \text{ S cm}^{-1}$ was found for the 30% 2-MCP-doped polymer blend electrolytes. The effect of solvent on the conductivity of solid polymer electrolytes were studied using various organic solvents such as *N,N*-dimethylformamide, acetonitrile, chlorobenzene, dimethylsulfoxide, 2-butanone, and isopropanol. The dielectric studies revealed that the 30% 2-MCP-doped PEO-PMMA-KI- I_2 electrolytes prepared by using DMF showed the highest dielectric constant as well as conductivity. The conversion efficiency of dye-sensitized solar cells fabricated using the optimized polymer electrolytes was found to be 3.0% under an illumination of 100 mW cm^{-2} . The solvent effect studies revealed that the solvent plays an important role on the conductivity of solid polymer electrolytes. Still the solvent evaporated by giving prolonged heat treatment under vacuum and a minute variation in ionic conductivity also beneficial for the electrochemical device applications.

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