

Research Article

Highly Conductive Redox-Couple Solid Polymer Electrolyte System: Blend-KI-I₂ for Dye-Sensitized Solar Cells

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Ionic conductivity of a redox-couple solid polymer electrolyte system, (1 - x) blend: x[0.9KI:0.1I₂] with x = 0–0.15 in weight fraction, is reported. A blend of poly(ethylene oxide) (abbreviated as PEO) and succinonitrile in equal weight fraction was used as a polymeric matrix instead of the PEO and succinonitrile because of its low-cost, electrical conductivity superior to the PEO, and thermal stability better than the succinonitrile. The electrolyte with x = 0.15 showed ionic conductivity of 7 × 10⁻⁴ S cm⁻¹ and iodine ion diffusivity of nearly 4 × 10⁻⁷ cm² s⁻¹ at 25°C. The conductivity and diffusivity values were nearly two orders of magnitude higher than those of the PEO-KI-I₂ due to the improved PEO crystallinity. It also exhibited dye-sensitized solar cell efficiency of 2.2% at 100 mW cm⁻², which is twice of the cell prepared using the PEO-KI-I₂ only.

1. Introduction

Following the invention of low-cost dye-sensitized solar cells (DSSCs), redox-couple solid polymer electrolytes have attracted considerable attention in recent years [1, 2]. These electrolytes eliminate the shortcomings of the liquid/gel electrolytes, such as leakage/evaporation of organic solvent especially at elevated temperatures, electrode corrosion, a need of hermetic sealing, and scale up of the manufacturing process. The PEO-MI-I₂ (M = Li, Na, or K) electrolyte-based DSSCs exhibited energy conversion efficiency (η) of 0.01–2% under the irradiation of 100 mW cm⁻² [2–6]. It was attributed to low ionic conductivity ($\sigma_{25^\circ\text{C}} \sim 10^{-6}$ – 10^{-5} S cm⁻¹) of electrolytes and poor interfacial contacts between the electrolyte, TiO₂, and dye at nanopores. The blending of PEO with a low molecular weight ether-based polymer improved the ionic conductivity, interfacial contacts, and, thus, the cell performance [3, 6, 7]. Dispersion of inorganic nanofiller into the electrolyte enhanced conductivity via providing the highly conductive space-charge regions and improved cell efficiency via penetration into the TiO₂ nanopores [6, 8].

Recently, DSSCs with succinonitrile-ionic liquid-based electrolytes have showed relatively high efficiency, 5–6.7%

at 25°C due to high ionic conductivity (10⁻⁴–10⁻³ S cm⁻¹), and iodine ion diffusivity ($\sim 10^{-6}$ cm² s⁻¹) of electrolytes along with better interfacial contacts [9, 10]. The succinonitrile (abbreviated as SN) acts as a solvent because of its low melting temperature (T_m , $\sim 54^\circ\text{C}$) and high dielectric constant (~ 55). It also provides vacancies for ion transport in its plastic crystal phase between -35°C and 54°C . However, low T_m -value ($\sim 40^\circ\text{C}$) and high-temperature instability of the electrolytes limited the use of the DSSCs for the indoor application only.

In a recent investigation, we showed that a blend of PEO and succinonitrile in equal weight fraction can also be utilized as a polymeric matrix [11]. The blend exhibited $\sigma_{25^\circ\text{C}}$ two orders of magnitude higher than that of the PEO and thermal stability better than the succinonitrile. The PEO offers dissociation/complexation of salt and segmental motion of polymeric chains. The succinonitrile is relatively cheap and provides vacancies for ion conduction. It also acts as organic filler that provides highly conductive free volume for ion transport [11–13]. In the present paper, PEO-SN blend is used as a matrix to synthesize a new low-cost and thermally stable fast ion conducting solid polymer electrolyte system, (1 - x)[PEO-SN]:x[0.9KI:0.1I₂], where 0 ≤ x ≤ 15

in weight fraction. KI is used as an ionic salt because K^+ ions assist in separating the polymeric chains for fast ion conduction [4]. The electrolytes are characterized by studying thermal, electrical, and photovoltaic properties.

2. Experimental

Highly pure Aldrich chemicals ($\geq 99\%$) were used for preparing the solid polymer electrolyte system. Molecular weight of the PEO was 10^6 g mol^{-1} . The precursors were dissolved in anhydrous acetonitrile (99.8%, Aldrich) and stirred at 60°C for 24 h resulting in homogeneous solution. The solution was poured on a Teflon Petri dish followed by drying in nitrogen gas atmosphere at room temperature for a week and further drying under vacuum at 28°C for a day. The PEO-SN blend with thickness $\sim 100 \mu\text{m}$ was translucent and mechanically good. The self-standing thick films of electrolytes were achievable up to $x = 0.15$ only, though salt was dissolvable up to $x = 0.2$.

For the thermal properties, a differential scanning calorimeter (MDSC 2910, TA Instruments) and a thermogravimetric analyzer (Hi Res TGA 2950, TA Instruments) were used with a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 gas atmosphere. Ionic conductivity of the films was measured using the impedance spectroscopy by a Solartron frequency response analyzer (1252A) coupled with SI 1287 electrochemical interface in a frequency range of 1 Hz–300 kHz. The electrolyte was sandwiched between two stainless steel plates with the help of a $300\text{-}\mu\text{m}$ thick Teflon spacer in a specially designed sample holder. A CHI600C voltammeter (CH instruments) together with an electrochemical cell (Figure 1) under a scan rate of 50 mV s^{-1} was employed for the iodine ion diffusivity measurement. DSSCs were prepared using conventional procedure with Solaronix-based Ti-Nanoxide D37 paste (TiO_2 particle size $\approx 37 \text{ nm}$), and 0.5 mM N719 dye solution [3]. An IVIVMSTAT electrochemical interface coupled with Newport solar simulator was used for the photovoltaic study.

3. Results and Discussion

Figure 2 shows differential scanning calorimetry (DSC) curves for the $(1-x)[\text{PEO-SN}] : x[0.9\text{KI} : 0.1\text{I}_2]$, where $x = 0-0.15$ in weight fraction. It portrayed endothermic peaks due to the melting temperature (T_m), crystal to plastic crystal phase transition (T_{pc}), and glass transition temperature (T_g) of the electrolytes, which are listed in Table 1 [9–13]. The blend ($x = 0$) exhibited intense peaks at -35°C (T_{pc}) and $\sim 30^\circ\text{C}$ (T_m) [11, 12]. The electrolyte with $x = 0.05$ showed a less intense T_m -peak at 29°C without the T_{pc} -peak. Further increase in x reduced the T_m -value with largely weak peak intensity. This is an indicative of a large decrease of the PEO crystallinity. The relative crystallinity (χ) can be quantified by the ratio of change in enthalpy (ΔH_m) of sample to that of the fully crystalline PEO ($\approx 193 \text{ J g}^{-1}$ [12]). As shown in Table 1, the values of ΔH_m and χ of the polymer electrolytes decreased with increasing x and reached to nearly zero for $x \geq 0.1$. This portrayed arrest of the amorphous phase for

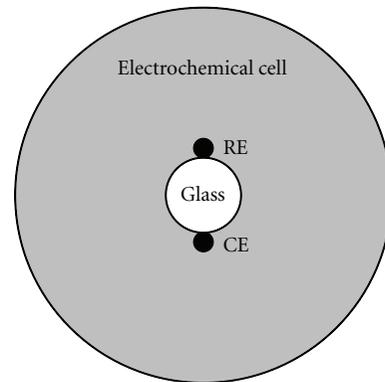


FIGURE 1: Electrochemical cell (top view) consisting of a glass cylinder with a $10\text{-}\mu\text{m}$ thick platinum wire as a working electrode (WE) at its center and 0.5-mm thick platinum wires as counter electrode (CE) and reference electrode (RE). The electrodes are on the same plane.

the $[\text{PEO-SN}]\text{-KI-I}_2$ electrolytes with $x \geq 0.1$. The PEO-KI-I₂ possessed χ of 36.8% [11]. It is due to the fact that interaction between the PEO chains, ionic salt, and plastic crystal extended the amorphous regions across the PEO with randomly oriented flexible polymeric chains [12, 13]. This observation is corroborative with the X-ray diffractometry (XRD) and polarized optical microscopy (POM) studies, data not shown. The XRD patterns and POM images of the electrolytes with $x \geq 0.1$ exhibited absence of the reflection peaks of the PEO and succinonitrile, and PEO spherulites, respectively. It is also worth mentioning that the TGA curves of the blend ($x = 0$) and electrolyte ($x = 0.15$) exhibited their thermal stability up to 100°C . Further increase in temperature started to sublime the succinonitrile with a complete loss near to its boiling temperature ($\sim 250^\circ\text{C}$) [11].

Table 1 also shows ionic conductivity ($\sigma_{25^\circ\text{C}}$) of the polymer electrolyte system, $(1-x)[\text{PEO-SN}] : x[0.9\text{KI} : 0.1\text{I}_2]$, where $x = 0-0.15$. The $\sigma_{25^\circ\text{C}}$ -value increased with increasing x due to an increase in ion concentration. The electrolyte with $x = 0.15$ ($[\text{O}]/[\text{K}^+] \approx 12$) exhibited the conductivity of $\sim 7 \times 10^{-4} \text{ S cm}^{-1}$, which is four orders of magnitude higher than that of the blend. In addition, it is two orders of magnitude higher than the conductivity ($\sim 2 \times 10^{-6} \text{ S cm}^{-1}$) of the $0.85\text{PEO} : 0.15[0.9\text{KI} : 0.1\text{I}_2]$ ($[\text{O}]/[\text{K}^+] \approx 24$), prepared identically using PEO. It is also more than an order of magnitude higher than the conductivity ($\sim 2 \times 10^{-5} \text{ S cm}^{-1}$) of the $0.75\text{PEO} : 0.25[0.9\text{KI} : 0.1\text{I}_2]$ electrolyte having $[\text{O}]/[\text{K}^+] \approx 12$ [5]. It suggests that the superior ion transport for the $0.85[\text{PEO-SN}] : 0.15[0.9\text{KI} : 0.1\text{I}_2]$ was provided most probably by the vacancies of the succinonitrile and extended free volumes.

This phenomenon is also depicted by the $\log \sigma - 1/T$ variations (Figure 3(a)) of the polymer electrolyte system, $(1-x)[\text{PEO-SN}] : x[0.9\text{KI} : 0.1\text{I}_2]$, where $x = 0-0.15$. It showed an increase in σ -value with increasing temperature forming a concave-type shape. This suggests that the ion transport is in the amorphous domains and coupled with

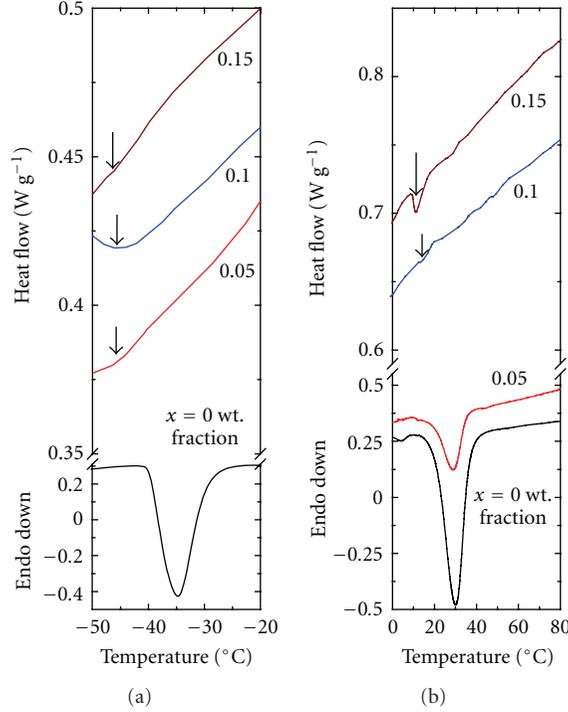


FIGURE 2: DSC curves for the $(1-x)[\text{PEO-SN}]:x[0.9\text{KI}:0.1\text{I}_2]$, where $x = 0-0.15$ in weight fraction.

TABLE 1: Melting temperature (T_m), crystal to plastic crystal phase transition (T_{pc}), glass transition temperature (T_g), change in enthalpy (ΔH_m), relative crystallinity (χ), ionic conductivity ($\sigma_{25^\circ\text{C}}$), preexponential factor (A), and pseudo activation energy (E_a) of the solid polymer electrolyte system, $(1-x)[\text{PEO-SN}]:x[0.9\text{KI}:0.1\text{I}_2]$.

Composition		T_m [$^\circ\text{C}$]	T_{pc} [$^\circ\text{C}$]	T_g [$^\circ\text{C}$]	ΔH_m [J g^{-1}]	χ [%]	$\sigma_{25^\circ\text{C}}$ [S cm^{-1}]	A [$\text{S cm}^{-1} \text{K}^{0.5}$]	E_a [eV]
x [wt. fraction]	$[\text{O}]/[\text{K}^+]$ [mole ratio]								
0	∞	30.1	-34.7	-60	48.7	25.2	1×10^{-8}	—	—
0.05	39.8	29.1	—	-46.4	16.3	8.4	3.6×10^{-5}	141	0.14
0.1	18.8	14.6	—	-46	~ 0.1	~ 0	6.5×10^{-4}	8.5	0.081
0.15	11.9	11.5	—	-46.1	~ 0.4	~ 0	7×10^{-4}	14.1	0.086

the polymer segmental motion. This can be expressed by the Vogel-Tamman-Fulcher empirical relation [13], $\sigma = AT^{-0.5}\exp[-E_a/k_B(T - T_0)]$. The notation A corresponds to the preexponential factor, T_0 is a temperature at which the free volume vanishes, and E_a is pseudo activation energy. As obvious in Figure 3(b), the electrolytes with $x = 0.05, 0.1,$ and 0.15 exhibited a linear variation between $\log \sigma T^{0.5}$ and $1/(T - T_0)$ with the coefficient of regression values greater than 0.995. The slope of the linear curve resulted in E_a value, which is shown in Table 1. The value of E_a decreased with increasing x with least value of ~ 0.08 eV for $x \geq 0.1$ indicating easy ion migration. This helps in improving the anionic diffusion required for the DSSC application, which has been discussed below.

Figure 4 shows steady-state voltammograms of the $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$ and $0.85\text{PEO}:0.15[0.9\text{KI}:0.1\text{I}_2]$ at $\sim 25^\circ\text{C}$. The former electrolyte showed limiting

cathodic current, $I_{ss,c}(I_3^-)$ of $\sim 1.3 \times 10^{-8}$ A and limiting anodic current, $I_{ss,a}(I^-)$ of $\sim 7.9 \times 10^{-8}$ A. These current values are relatively higher to those of the $0.85\text{PEO}:0.15[0.9\text{KI}:0.1\text{I}_2]$, $I_{ss,c}(I_3^-) \sim 8.8 \times 10^{-11}$ A, and $I_{ss,a}(I^-) \sim 1 \times 10^{-9}$ A, suggesting improved I_3^- and I^- ions diffusion. The apparent diffusion coefficient (D_{app}) of anions was estimated using an expression, $D_{app} = I_{ss,c}/4nC_rF$ [9, 10]. The notation n is a number of electrons per molecule, C is the bulk concentration, r is the radius of the microelectrode, and F is the Faraday's constant. The D_{app} of the $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$ was calculated as $\sim 4.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for I_3^- and $\sim 4.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for I^- . The $0.85\text{PEO}:0.15[0.9\text{KI}:0.1\text{I}_2]$ portrayed $D_{app}(I_3^-)$ of $\sim 2.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $D_{app}(I^-)$ of $\sim 4.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Thus, the PEO-SN blend-based electrolyte possessed better anionic diffusivity due to the fact that the succinonitrile provides highly conductive free volumes for easy ion migration.

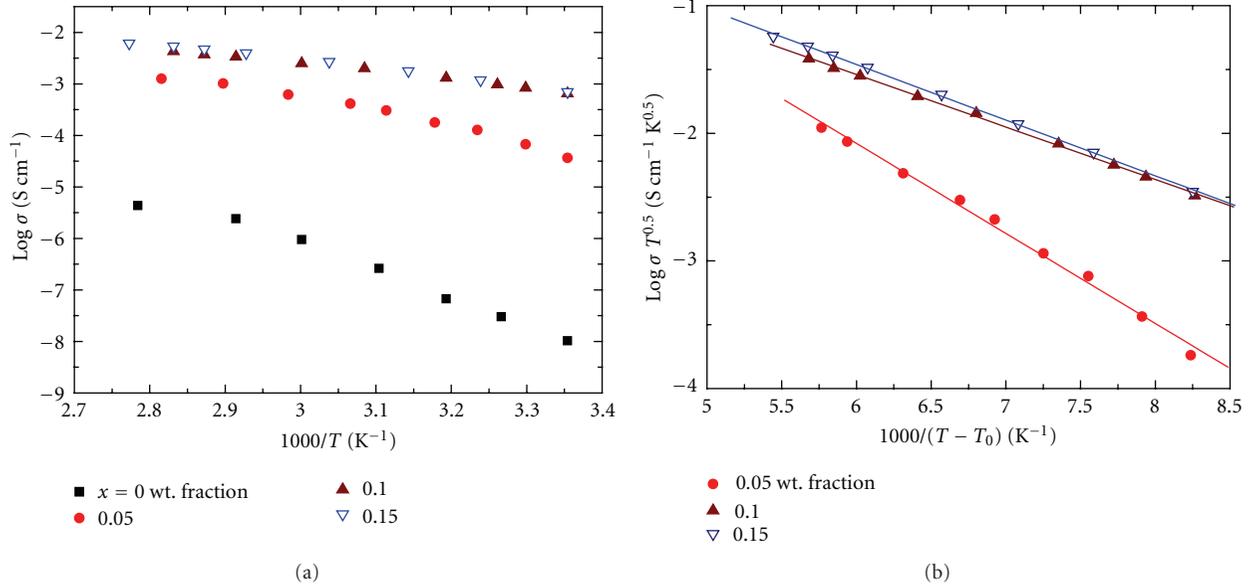


FIGURE 3: (a) $\text{Log } \sigma - 1/T$ and (b) $\text{log } \sigma T^{0.5} - 1/(T - T_0)$ plots of the $(1-x)[\text{PEO-SN}]:x[0.9\text{KI}:0.1\text{I}_2]$, where $x = 0-0.15$ in weight fraction.

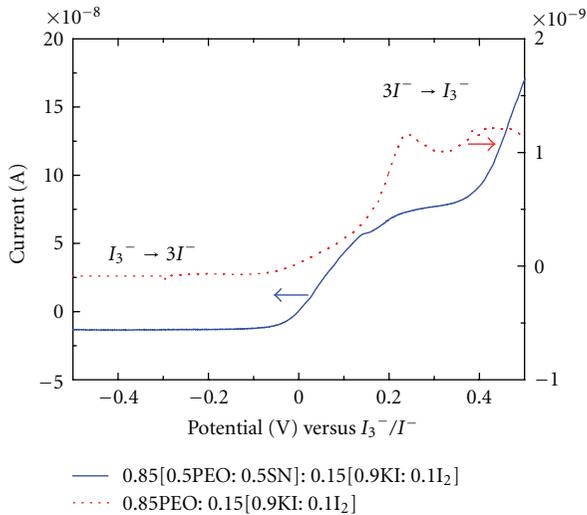


FIGURE 4: Steady-state voltammograms of the $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$ and $0.85\text{PEO}:0.15[0.9\text{KI}:0.1\text{I}_2]$.

Figure 5 shows photocurrent density-voltage curve of the DSSCs fabricated using the $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$. The measurement was carried out under solar irradiation of 100 mW cm^{-2} (AM 1.5) at $\sim 25^\circ\text{C}$. The cell exhibited short-circuit current density (J_{sc}) of 6.5 mA cm^{-2} , open-circuit voltage (V_{oc}) of 0.7 V , fill-factor (FF) of 49%, and cell efficiency (η) of 2.2%. For the $0.75\text{PEO}:0.25\text{KI}/0.025\text{I}_2$, having a similar value of $[\text{O}]/[\text{K}^+]$, J_{sc} , V_{oc} , FF, and η were achieved as 2.47 mA cm^{-2} , 0.82 V , 50.8%, and 1.04%, respectively [5]. Thus, the $[\text{PEO-SN}]-[\text{KI-I}_2]$ -based DSSCs exhibited better efficiency, which is due to the improved ionic conductivity and anionic diffusivity with the better interfacial contacts [6–10].

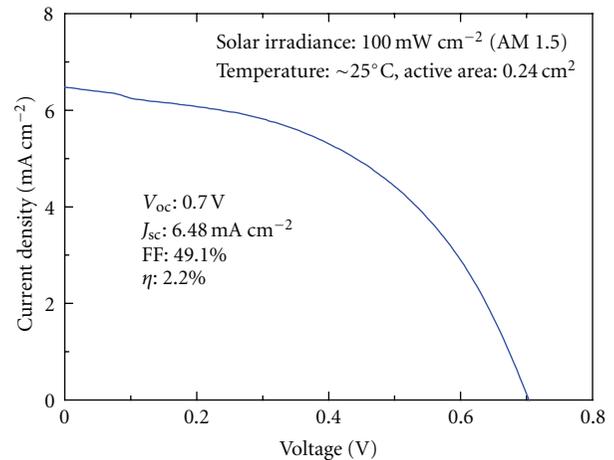


FIGURE 5: Current density-voltage curve of the DSSC fabricated using the $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$.

4. Conclusion

A new fast ion conducting redox-couple solid polymer electrolyte system, $(1-x)[\text{PEO-SN}]:x[0.9\text{KI}:0.1\text{I}_2]$, where $0 \leq x \leq 0.15$, was synthesized using a low-cost and thermally stable $0.5\text{PEO}:0.5\text{SN}$ blend as a polymeric matrix. The $0.85[\text{PEO-SN}]:0.15[0.9\text{KI}:0.1\text{I}_2]$ exhibited ionic conductivity, anionic diffusivity, and cell efficiency better than those of the $0.85\text{PEO}:0.15[0.9\text{KI}:0.1\text{I}_2]$. This was attributed to the extension of amorphous regions across the PEO and availability of vacancies for ion transport by the succinonitrile as well as the improved interfacial contacts between the electrolyte, TiO_2 , and dye at nanopores.

Acknowledgments

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