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Research Article

Polyvinylidene fluoride based gel polymer electrolyte to be used in solar energy to electrical energy conversion

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Abstract

There is a great attention towards fulfilling energy requirement via renewable energy sources. Solar energy is one of the uprising renewable energy sources for the planet earth. Dye sensitized solar cells (DSSCs) have been identified as a promising technology to harvest solar energy and to convert that to electricity. In this study, it was attempted to optimize the composition of a gel polymer electrolyte consisting with polyvinylidene fluoride (PVdF), ethylene carbonate (EC), propylene carbonate (PC), tetrahexylammonium iodide (Hex₄NI) and iodide (I₂) to be utilized for DSSC application. The composition was fine tuned to get the highest conductivity by varying the salt concentration. The composition, 100 PVdF / 400 EC / 400 PC / 150 Hex₄NI / 7.3 I₂ exhibited the highest conductivity of $3.43 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature. Sample was purely an anionic conductor. DSSCs were fabricated in the configuration, FTO / TiO₂ / Dye / GPE / Pt / FTO. The open circuit voltage and short circuit current density were 799 mV and 1.06 mA respectively. The calculated fill factor was 0.62 and the efficiency was 2.08% .

Keywords: Gel polymer electrolyte, Dye sensitized solar cell, polyvinylidene fluoride

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1. INTRODUCTION

Due to the warning of doubling the energy requirement of the globe within next few years and dreadful climatic consequences of the green house effect by fossil fuel combustion, seeking alternative renewable energy sources has become an urgent requirement. Upon the first report made by M. Gratzel in 1991 about dye sensitized solar cells (DSSCs), an intense interest aroused to develop them all over the world owing to some of their fascinating properties like low cost, simple preparation procedure and benign effect on the environment.¹

DSSCs are fallen into the third generation of photovoltaic technology. Conventional solar cells are based on crystalline silicon and depend on P-N junction to separate photo generated charge carriers. In DSSCs, light absorption is separated from the charge carrier transport.² Even the solar power conversion efficiencies of DSSCs are lower than that of silicon based solar cells, there is a great potential to improve their performance. Since the work of Gratzel, many attempts have been put forward to develop DSSCs but most were consisting with a liquid electrolyte. The presence of a liquid electrolyte has given rise to numerous drawbacks such as leakage, volatilization, corrosion, photo degradation and low flexibility of device fabrication with respect to shape.³ These have led to replace liquid electrolytes by solid electrolytes. Mainly, due to the lower conductivity of solid electrolytes, attention has been diverted towards polymer electrolytes which are known to be lying in between solid electrolytes and liquid electrolytes.

As polymer electrolytes are also suffering from poor ambient temperature conductivities, gel polymer electrolytes (GPEs) have received an enormous attention to be employed for various applications such as batteries, artificial muscles, DSSCs, super capacitors and electrochromic devices.^{4,5} In general, a DSSC consists of a transparent conductive oxide glass, a nano porous semi conducting layer, a dye layer bonded on to the semiconducting layer, an electrolyte with an iodide (I⁻)/ triiodide (I₃⁻) redox couple and a counter electrode.⁶ Presence of redox couple is really important for the better performance of a DSSC. It participates for redox reaction while shuttling between the photo electrode and the counter electrode. Many have reported that use of bulky cation iodide salts are much suitable to be used for electrolytes as they show higher iodide conductivity due to large cation of which the mobility is extremely lower than iodide ions.

In this study, a DSSC was fabricated using the GPE consisting with polyvinylidene fluoride (PVdF), ethylene carbonate (EC), propylene carbonate (PC), tetrahexylammonium iodide (Hex₄NI) and iodide (I₂). This salt, Hex₄NI has been used to prepare GPEs for DSSCs with the polymers such as polyethylene oxide (PEO) and polyacrylonitrile (PAN) by several groups.^{7,8}

2. METHODS AND MATERIALS

2.1 Preparation of GPE

Polyvinylidene fluoride (PVdF, MW 534,000), ethylene carbonate (EC, 98%), propylene carbonate (PC, 98%), tetrahexylammonium iodide (Hex₄NI, 99%) and iodide (I₂) were used as received from ALDRICH. Required amounts of the materials were weighed and magnetic stirring was done for about 1 hour until all are mixed thoroughly. The resulting homogeneous solution was heated at 80 °C for 1 hour. Thereby, it was possible to get a viscous solution which was pressed in between two well cleaned glass plates. Upon cooling, a thin bubble free film could be obtained.

2.2 Optimizing the composition of GPE

Samples were prepared varying the salt concentration. Weight of I₂ was kept as the molar ratio of the salt : I₂ equals 10 : 1.

2.3 AC conductivity measurements

A sample of circular shape was cut from the electrolyte film and it was loaded inside a spring loaded sample holder in between two stainless steel (SS) electrodes. Impedance measurements were taken from room temperature to 60 °C in the frequency range 37 kHz – 0.01 Hz using a METROHM 101 frequency response analyser.

2.4 DC polarization test

A circular shape sample was loaded as explained in section 2.3 to perform the DC polarization test under blocking electrodes. Current variation with time was monitored applying a DC bias voltage of 1 V. A similar setup was used with iodide electrodes for the DC polarization test under non-blocking electrodes.

2.5 Preparation of photo anode

First, fluorine doped tin oxide (FTO) glass strips were cleaned well. Titanium dioxide (TiO₂) paste was prepared by grinding TiO₂ (Degussa P-25) for few minutes alone. Few drops of acetic acid and ethanol were mixed in during grinding process. Then, the resulting slurry was spread on an active area of 0.25 cm² on FTO glass strips using doctor blade method. The electrodes were heated at 450 °C for 45 minutes. Those nano porous electrodes were allowed to cool down to room temperature. Thereafter, they were dipped in ethanolic Ruthenium dye solution for dye absorption overnight.

2.6 Fabrication and characterization of the DSSC

The GPE that had shown the highest conductivity was used to fabricate the DSSC. It was sandwiched in between the TiO₂/Dye photo anode and Pt counter electrode. The final configuration of the DSSCs was in the form, FTO / TiO₂ / Dye / GPE / Pt / FTO. The photo current density – voltage (J_{SC}-V) characteristics of the cells were measured under 100 mW/cm² illumination.

3. RESULTS AND DISCUSSION

Impedance data analysis was done with the NOVA programme using corresponding equivalent circuits. The conductivity was calculated using the equation,

$$\sigma = (1/R_b)(t/A) \quad (1)$$

where R_b is the bulk electrolyte resistance, t and A are thickness and area of the electrolyte film respectively.

Room temperature (28 °C) conductivity (σ_{RT}) variation with salt concentration is shown in Figure 1. It is seen that with increasing salt concentration, conductivity increases. After the salt concentration of 150 (by weight), conductivity decreases. This hints that there should be some competitive factors to govern the variation of conductivity with salt concentration. It is a well-accepted fact that conductivity depends on the charge carrier concentration as well as their mobility. When increasing the salt concentration, it is natural

that charge carrier concentration increases giving rise to higher conductivities. Further increment of salt concentration may increase the viscosity of the medium disturbing the charge mobility. In addition, more and more charge aggregates can form at high salt concentrations which do not assist for conductivity.⁹ These factors may reduce conductivity.

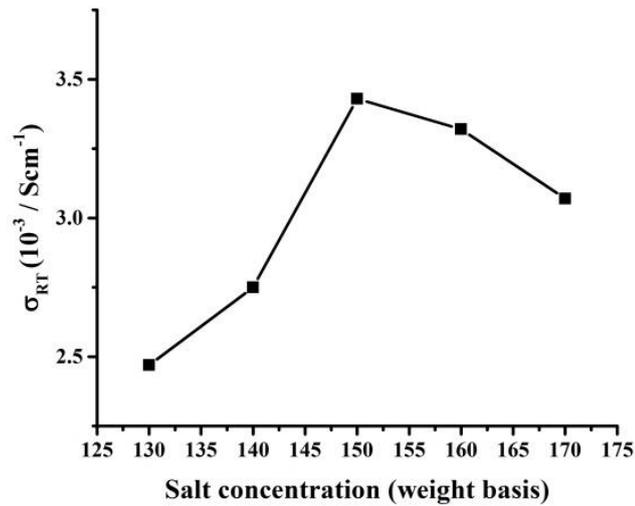


Figure 1: Room temperature conductivity variation with the salt concentration

Figure 2 shows the variation of conductivity with different salt concentrations at different temperatures.

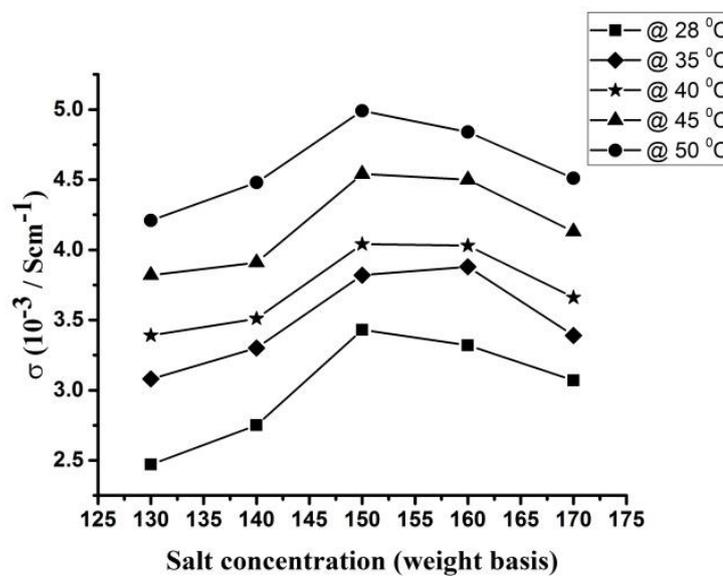


Figure 2: Variation of the conductivity with the salt concentration at different temperatures

The behavior of the curves exhibit the fact that when increasing the temperature, conductivity increases substantially. A possible reason may be the increasing of mobility of charge carriers by gaining energy upon increasing temperature. Another feature that can be elucidated is even upon increasing temperature, the maximum conductivity is available with the salt concentration 150 (by weight). Hence, it is well proven that the salt concentration of 150 (by weight) gives the highest conductivity. The optimum composition that results the highest conductivity of $3.43 \times 10^{-3} \text{ Scm}^{-1}$ is 100 PVdF / 400 EC / 400 PC / 150 Hex₄NI / 7.3 I₂. The order 10^{-3} is a satisfactory value to be employed this particular electrolyte for ambient temperature applications. A GPE based on PVdF, EC, PC and the salt 1methyl 3propyl Immidazolium Iodide has been reported by us previously with a room temperature conductivity of $3.55 \times 10^{-3} \text{ Scm}^{-1}$.¹⁰ 1methyl 3propyl Immidazolium Iodide is considered to be in the group of ionic liquids which are known to have higher conductivities. Due to this reason, it can show a higher conductivity than the present system. But, with respect to mechanical properties, the present system is far more better. When preparing the GPE having 1methyl 3propyl Immidazolium Iodide, the glass plates with the hot electrolyte mixture were left in a vacuum desiccator overnight to obtain the film. It was not possible to separate the plates soon after hot pressing as with the present system. S. Rajendran *et al.* have carried out investigations on a GPE with PVdF, EC, PC, LiClO₄ and LiCF₃SO₃.¹¹ All of those systems have exhibited lower conductivity values than the present system.

DC polarization test results obtained with blocking electrodes are shown in Figure 3. The ionic transference number (t_i) was calculated using the following equation.

$$t_i = (I_t - I_s) / I_t \quad (2)$$

Here, I_t is the total current, I_s is the saturated current.

The initial current (I_t) which is due to ions and electrons has dropped quickly and has reached a stable value (I_s) due to the electrons. The abrupt drop of current is due to the blocking nature of SS electrodes towards ions. Soon after polarization of ions, the current due to electrons is existing. The value of t_i is 0.9 which clearly indicates that the electrolyte sample is predominantly an ionic conductor.¹²

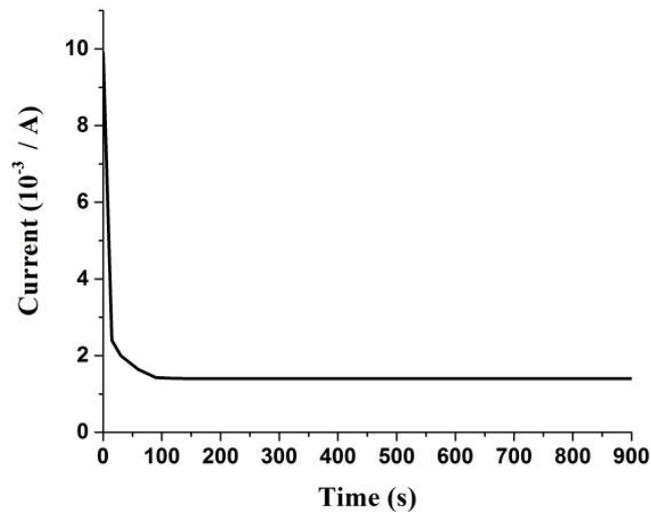


Figure 3: DC polarization test results obtained with blocking electrodes

Figure 4 shows the variation of current with time when using the non-blocking electrodes.

The anion transference number (t) was calculated using the following equation¹³.

$$t = I_s / I_t \quad (3)$$

I_t is the total current due to cations and anions and I_s is the saturated current due to anions.

In this test, initial current has a very small drop followed by a stable state. The initial current is due to the cations and anions in the system whereas the saturated current is due to anions as the electrodes are blocking cations. The small drop of initial current hints the fact that cations do not provide a considerable contribution. Therefore, it can be inferred that the system under study is a good anion or iodide conductor. This further confirms the fact that when the cation of the salt is large, anions show a higher mobility. This is one of the most essential requirements for the electrolyte to be used for DSSCs.

In iodide/triiodide based DSSCs, there is a possibility for triiodide to get recombined with electrons ejected to TiO_2 . This is negatively affecting the performance of DSSCs by lowering Fermi level of TiO_2 and in turn V_{oc} . When the cation of the salt is large in size,

triiodide diffusion is low and hence, there is no probability for the recombination. So, Fermi level of TiO₂ increases and as a result, V_{oc} is also increasing.¹⁴

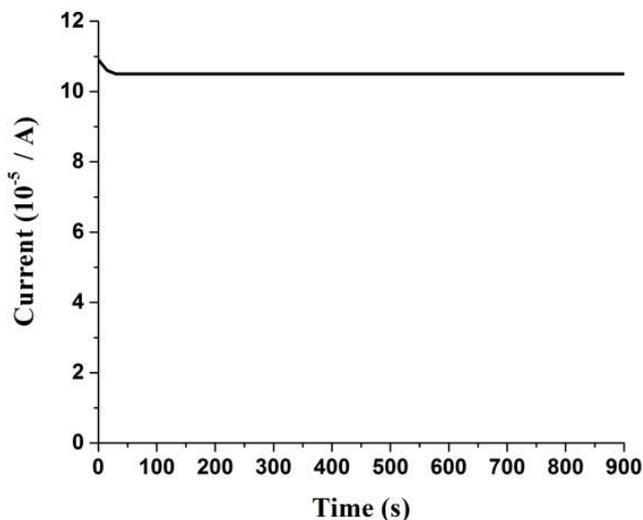


Figure 4: DC polarization test results obtained with non blocking electrodes

Figure 5 shows the J_{sc}-V characteristic curve for the DSSC fabricated with the electrolyte having the maximum conductivity.

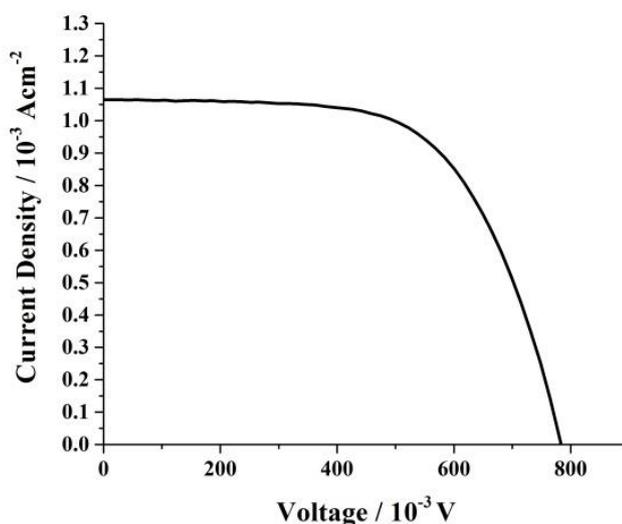


Figure 5: I-V characteristics of the DSSC in the configuration, FTO/TiO₂/Dye/GPE/Pt/FTO

The open circuit voltage and short circuit current density were 799 mV and 1.06 mA respectively. The DSSC we have fabricated with an ionic liquid has shown an open circuit voltage lower than the present system.¹⁰

Fill factor (FF) and efficiency (η) were calculated using the equations given below.

$$FF = J_{\max} \cdot V_{\max} / J_{sc} \cdot V_{oc}$$

$$\eta = (J_{\max} \cdot V_{\max} / P_{in}) 100\%$$

where J_{\max} and V_{\max} are respective current density and voltage at the maximum power point, J_{sc} and V_{oc} are short circuit current density and open circuit voltage, P_{in} is the incident power.^{15,16}

The calculated value of the FF was 0.62 whereas the efficiency was 2.08. The system we have reported with PVdF, EC, PC and the salt 1methyl 3propyl Immidazolium Iodide has resulted a FF of 0.58 which is slightly lower even the conductivity value is higher than the present system¹⁰. The performance characteristics are somewhat attractive and need further studies to improve them. PVdF has been largely used for batteries.^{17,18} And also, the use of PVdF with Hex₄NI has not been considered for DSSCs as per the literature survey. PAN and PEO have been used for fabrication of DSSCs by Bandara *et al.* with this salt.⁸ In terms of conductivity as well as cell performance, the present study shows better values. Hence, this study may boost the interest on the selected combination of PVdF, EC, PC, and Hex₄NI to be employed for DSSCs.

4. CONCLUSION

By using PVdF, EC, PC, Hex₄NI and I₂, thin and mechanically stable electrolyte films can be prepared. By varying the salt concentration, the optimum composition that results the highest conductivity of $3.43 \times 10^{-3} \text{ Scm}^{-1}$ was determined as 100 PVdF / 400 EC / 400 PC / 150 Hex₄NI / 7.3 I₂. Even upon increasing temperature, this salt concentration yields the highest conductivity irrespective of the fact that conductivity increases with increasing temperature. The resulting sample is a good ionic conductor having more contribution from anions. The electrolyte under investigation is an ideal candidate for DSSCs.

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