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Dye-sensitized solar cells based on electrospun polyacrylonitrile (PAN) nanofibre membrane gel electrolyte

M.A.K.L. Dissanayake[a,d,e,*], H.K.D.W.M.N.R. Divarathne[a,e], C.A. Thotawatthage[a], C.B. Dissanayake[a], G.K.R. Senadeera[a,b], B.M.R. Bandara[c]

[a] Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka
[b] Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka
[c] Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka
[d] Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka
[e] Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

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ABSTRACT

Dye Sensitized Solar Cells (DSSCs) based on electrospun nanofibre membrane electrolytes offer several advantages over liquid electrolyte based solar cells. Nanofibre membranes having different thicknesses were prepared by electrospinning on platinum electrodes from a 11 wt% solution of polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF) at an applied voltage of 8 kV. The membranes were then activated by immersing in a solution containing potassium iodide (KI) (0.06 g), propylene carbonate (PC) (0.8 g) and iodine (I_2) (0.0092 g) for 30 minutes to obtain "gel" type membrane electrolytes with different thicknesses. These nanofibre membrane electrolytes were used to fabricate quasi-solid state (gel) DSSCs and the performance of these solar cells were compared with DSSCs fabricated with liquid electrolyte (KI:PC:I_2) and conventional PAN based gel electrolyte (PAN:KI:PC:I_2). DSSC with nanofibre membrane electrolyte of thickness 9.14 μm showed the highest light-to-electricity conversion efficiency of 5.2% whereas an identical cell based on corresponding liquid electrolyte showed an efficiency of 5.3%. The open circuit voltage (V_{OC}), short circuit current density (J_{SC}) and fill factor for the solar cell based on this electrolyte was 0.67 V, 13.31 mA cm^{-2} and 59% respectively at an incident light intensity of 1000 W m^{-2} with a 1.5 AM filter.

1. Introduction

Among the sources of renewable energy, the solar energy is considered to be the most promising. Therefore, the development of dye sensitized solar cells (DSSCs) plays a major role in the research area of solar energy conversion because of their low production cost and simple preparation techniques [1,2]. DSSCs using liquid electrolytes have received significant attention because of their high power conversion efficiencies [3,4]. However, due to a number of major drawbacks in these DSSCs fabricated with organic liquid electrolytes which include the lack of long term stability, liquid leakage, electrode corrosion, dye degradation and volatility of liquid electrolytes, many research groups have been searching for alternative materials to replace the liquid electrolyte [5]. Solid polymer electrolytes and gel polymer electrolytes are some of the alternative materials that are being developed and tested for DSSC applications. Although solid state electrolyte based DSSCs can solve some of the above drawbacks, their conversion efficiencies have been rather low to make practical devices. Therefore, during recent years development of quasi-solid state or gel electrolytes where a liquid electrolyte is "entrapped" within a host polymer matrix such as those made from polyacrylonitrile (PAN), poly(vinylidenefluoride (PVdF) and polymethylmethacrylate (PMMA) have drawn the attention of the DSSC community [6–9]. These gel electrolytes, while exhibiting almost liquid like ionic conductivities, offer better mechanical and chemical stability for the DSSCs. Another possible approach to develop alternative quasi-solid state electrolytes suitable for DSSCs is by using polymer nanofibre electrolyte membranes activated by a suitable liquid electrolyte [10]. However, reported work on this line of research is scanty. In the present study, we have successfully synthesized PAN nanofibre membranes by electrospinning technique and made

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* Corresponding author. Institute of Fundamental Studies Hantana Road Kandy Sri Lanka Website: www.ifs.ac.lk. Tel.: +94 81 2232002/+94 777 130667; fax: +94 81 2232131.
E-mail address: makldis@yahoo.com (M.A.K.L. Dissanayake).

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quasi-solid state electrolytes by incorporating a liquid electrolyte within the nanofibre matrix and used them for the fabrication of DSSCs.

Polymeric nanofibres can be processed by a number of different techniques such as drawing, template synthesis, phase separation, self-assembly and electrospinning. Among these techniques electrospinning is probably the simplest and low cost method for making ultrathin diameter nanofibres where the fibre structures can be varied by varying the electrospinning parameters.

Electrospinning process was first studied by Zeleny in 1914 and patented by Formhals in 1934 [11,12]. This process can create nanofibres through an electrically charged jet of polymer solution or polymer melt. The simplest form of the electrospinning process consists of a pipette to hold the polymer solution, two electrodes and a DC voltage supply in the kV range. Due to the high voltage, the polymer solution drops formed at the tip of the pipette is drawn into fibres and these fibres become bent because polymer jet is electrically charged [13].

In the present study, we have successfully fabricated the DSSCs using electrospun PAN polymer nanofibre membranes with different thicknesses and optimized the preparation conditions by varying the electrospinning parameters. Photovoltaic performance of the DSSCs incorporating theses nanofibre membranes was studied by using a solar simulator under the illumination of 1000 Wm^{-2}. The results were compared with the conventional liquid electrolyte and conventional gel electrolyte based DSSCs. The current onsets of DSSCs with these three types of electrolytes under reverse bias condition were also investigated. The interfacial charge transfer resistances were investigated by electrochemical impedance spectroscopy measurements (EIS).

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Avg. Mw 150,000) was purchased from Sigma Aldrich and N, N-dimethylformamide (DMF), propylene carbonate (PC), potassium iodide (KI) and iodine (I_2) with purity >98% were purchased from Fluka. Fluorine-doped SnO_2-layered (FTO) glass (sheet resistance 12 Ω/sq), Ruthenium dye (N719) and commercially available titania (TiO_2) paste were purchased from Solaronix SA.

2.2. Preparation of the PAN nanofibre membranes

A NABOND electrospinning system (NaBond Technologies, Hong Kong) was used to prepare the PAN nanofibre membranes. The solution for electrospinning was prepared from a 11 wt% solution of PAN in DMF heated at 140 °C with constant stirring to form a transparent homogeneous polymer solution, which was then cooled to room temperature. The resulting polymer solution was used for electrospinning and 8 kV dc voltage was applied between the spinneret and the drum collector. The flow rate of the polymer solution was adjusted to 2 ml/h by using a syringe pump. The electrospun PAN nanofibres were then collected onto a grounded, polished Pt plates which were attached to the drum collector having a speed of 270 rpm. Half of the area of each Pt plate was covered by an aluminum foil so that the active area of a Pt plate for deposition of the nanofibres was 2 cm^2. The tip-to-collector distance was fixed at 6.5 cm. To vary the thickness of the nanofibre membrane the duration of electrospinning was varied. In order to check the film thickness the films were also deposited on aluminum foils under the same experimental conditions.

2.3. Fabrication of the quasi-solid state DSSCs

The TiO_2 electrode film of thickness about 12 μm was prepared by spreading titania paste (Ti-Nanoxide D) on a pre-cleaned FTO plate using the doctor blade technique and sintered at 450 °C for 45 min. The FTO glass with TiO_2 film was subsequently immersed in an ethanolic solution of N719 dye of 0.3 mM at room temperature for 24 h. For the counter electrode a PAN nanofibre deposited Pt plate was used. The electrolyte solution was made by dissolving 0.06 g of KI and 0.0092 g of I_2 in 0.8 g of PC. Two drops of the electrolyte solution was placed on the PAN nanofibre membrane deposited on Pt electrode and was kept in ambient atmosphere for about 30 min in order for the membrane to “swell” by absorbing the electrolyte solution and form the quasi-solid state (gel) electrolyte film. Excess solution was carefully wiped off to minimize the presence of “free” liquid electrolyte. The quasi-solid state DSSCs of configuration, FTO/TiO_2/electrospun nanofibre membrane gel electrolyte (NFGEL)/Pt/FTO, were fabricated by keeping together the Pt electrode containing the membrane electrolyte and the TiO_2 electrode (Figure 1). In order to compare the device performance, DSSCs were also fabricated with liquid electrolyte without PAN (LEL) and conventional gel electrolyte with PAN (GEL). Each resulting cell had an active area of 0.25 cm^2.

2.4. Measurements

The morphologies of the electrospun nanofibre membranes were observed by the Scanning Electron Microscopy (SEM; JEOL JSM-6510LV). The thickness of the fibre films were determined by using the SEM images of the cross section of the fibre films. Photovoltaic characteristics of the DSSCs were measured by using a home-made computer-controlled solar simulator which was coupled to a Keithly 2000 multimeter with Potentiostat/galvanostat HA-301 under the illumination of 1000 W m^{-2} using the Xenon 500 lamp with an AM 1.5 filter. The incident light intensities were calibrated by using a Si reference cell (HAMAMATSU S1227-1010BQ silicon photodiode) and International Light Technologies research radiometer (ILT1700). Electrochemical Impedance Spectroscopy(EIS) measurements were performed on the DSSCs using the Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N coupled to a FRA32 M Frequency Response Analyzer (FRA) covering the 2 Hz to 100 kHz frequency range and using an AC voltage signal of 10 mV. These measurements were carried out under the illumination of 1000 W m^{-2} using the same solar simulator. Dark I-V measurements were obtained for each solar cell using AutoLab PGSTAT 128 N.

3. Results and Discussion

3.1. Electrospun PAN nanomembrane-based gel electrolyte (NFGEL)

In the electrospinning method there are several variable parameters such as the voltage applied between the needle tip and the collector plate, tip-to-collector distance (TCD), flow rate, concentration and the viscosity of the polymer solution which can directly affect the morphology porosity and the diameter of the electrospun nanofibres.

Figure 2 shows the SEM images of the top view and the cross sectional view of an electrospun PAN nanofibre membrane which was fabricated under the optimized conditions of 11 wt% of PAN solution, 8 kV of applied voltage, 6.5 cm of TCD and 2 ml/h of flow rate. As seen from these pictures, the PAN membrane has a three dimensional network structure with extremely high porosity consisting of thin fibres having diameter of about 500 - 900 nm. Also

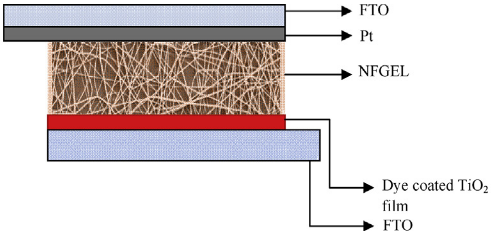

Fig. 1. Schematic diagram of the solar cell fabricated using the PAN nanofibre based gel electrolyte (NFGEL).

this membrane consists of a large number of interconnected pores. Therefore the membrane should be able to uptake a large amount of electrolyte solution in its pores and due to its three dimensional network structure with numerous physical cross linking points, electrospun membrane has sufficiently high mechanical strength as well [14,15].

3.2. Photovoltaic Performance

Photovoltaic parameters of the DSSCs with (A) the quasi-solid-state (gel) electrolyte based on PAN membrane having different thicknesses (NFGEL), (B) a conventional liquid electrolyte having the same composition but without PAN (LEL), and (C) a conventional PAN-based gel electrolyte having the same composition (GEL) are summarized in Table 1.

From Table 1, it can be seen that the maximum efficiency (η) of 5.2%, J_{SC} of 13.31 mA cm^{-2}, V_{OC} of 0.67 V and FF of 59% were obtained for the best DSSC fabricated with electrospun nanofibre membrane electrolyte (NFGEL) having a thickness of 9.14 μm. As shown in Figure 3, the variation of short circuit photocurrent density (J_{sc}) of I^-/I_3^- ion based DSSC with the thickness of the PAN nanofibre membrane appears to be directly related to the iodide ion conductivity in the electrolyte medium. Similar correlation between the J_{SC} and iodide ion conductivity has been recently reported for several other DSSC systems [16–18]. When increasing the thickness of the fibre membrane up to 9.14 μm, the J_{SC} value increases and goes through the maximum at 9.14 μm and then decreases. The efficiency follows a similar variation with membrane thickness. When the thickness of the fibre membrane is small (3.41 μm), the number of pores in the fibre membrane is low and therefore the amount of the electrolyte solution the membrane can uptake is also low; Thus, the amount of electrolyte solution per unit area is low and hence the electrolyte in contact with the dyed TiO_2 electrode is also low, leading to a low value of the J_{SC} due to the low rate of dye regeneration. When the thickness of the fibre membrane is increased to 9.14 μm, the number of cross linking points also increases providing extra mechanical strength to the membrane. Due to the increased number of pores and pore space, the membrane is now able to uptake a larger amount of electrolyte solution with increased penetration in to the TiO_2 nanopore structure leading to higher dye regeneration and the solar cell can now deliver higher photocurrent densities. When this optimum membrane thickness is reached, solar cell shows the maximum J_{SC} value. The current density in the DSSC with 5.43 μm thick membrane lies in between those corresponding to 3.41 μm and 9.14 μm. After reaching the maximum J_{SC} value of 13.31 mA cm^{-2} at 9.14 μm thickness, the current density starts to drop gradually possibly due to the more dense nanofibre matrix and blocking effect which reduces the mobility of I^-/I_3^- ions within the electrolyte. Even the highest J_{SC} value of the DSSC with optimum thickness of the nanofibre electrolyte is slightly lower compared to that of the liquid electrolyte based solar cell. This lower J_{SC} value is very likely due to the reduction in the penetration of the NFGEL electrolyte into the dyed TiO_2 electrode (lower dye regeneration) and the reduced mobility of iodide ions caused by the presence the nanofibre matrix.

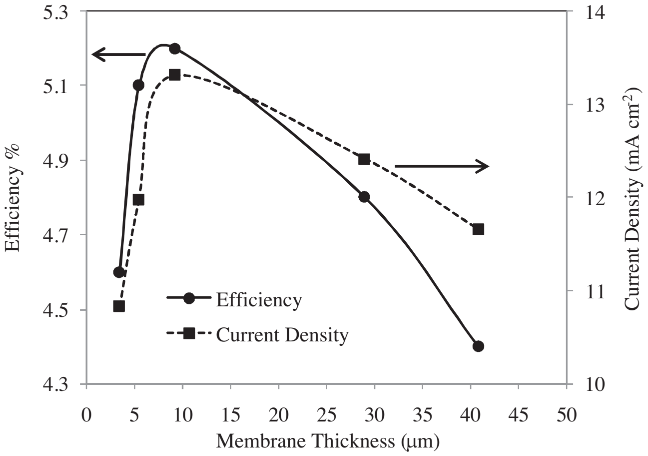

Fig. 3. Variation of the current density and efficiency of DSSCs as a function of PAN membrane thickness.

The comparison of photo current density vs.voltage curves for the solar devices under the same illumination conditions comprising with electrolytes, 9.14 μm NFGEL, LEL and GEL electrolytes are shown in Figure 4.

From Table 1, it can be seen that an enhanced V_{OC} value and a reduced J_{SC} value, compared with the corresponding values of the DSSC with liquid electolyte (LEL), were obtained for the DSSC with electrospun membrane gel electrolyte (NFGEL). However, for the conventional gel electrolyte (GEL) based DSSCs, all the photovolatic parameters including η showed lower values than with the DSSCs with NFGEL electrolyte. This is possibly because the NFGEL electrolyte is actually a solution electrolyte soaked in a nanofibre matrix, having a large porosity and exhibiting almost liquid like

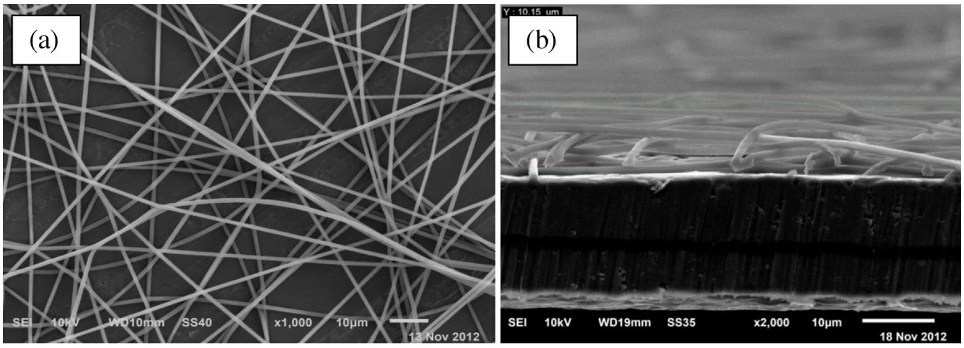

Fig. 2. SEM images of the electrospun PAN membrane (a) top view of the membrane (b) cross section of the fibre membrane on top of the aluminium foil.

Table 1
Photovoltaic parameters of the DSSCs with (A) with the quasi-solid-state electrolyte based on PAN membrane having different thicknesses, (B) a conventional liquid electrolyte having the same composition but without PAN, and (C) conventional PAN-based gel electrolyte having the same composition.

	PAN nanifibre membrane gel electrolyte (NFGEL)*					Liquid electrolyte (LEL)*	Gel electrolyte (GEL)*
Thickness of the PAN nanofibre membrane(μm)	3.41	5.43	**9.14**	28.89	40.71		
V_{OC} (V)	0.68	0.67	**0.67**	0.65	0.65	0.62	0.64
J_{SC} (mA cm^{-2})	10.83	11.97	**13.31**	12.41	11.66	13.42	12.03
FF (%)	63	63	**59**	60	59	64	56
η (%)	4.6	5.1	**5.2**	4.8	4.4	5.3	4.3

*Electrolyte compositions:
NFGEL: PC (0.8 g) + KI (0.06 g) + I_2 (0.0092 g) + PAN nanofibre membrane
LEL: PC (0.8 g) + KI (0.06 g) + I_2 (0.0092 g)
GEL: PC (0.8 g) + KI (0.06 g) + I_2 (0.0092 g) + PAN (0.1 g)

ionic conductivitiy but having a quasi-solid structure, while the conventional PAN based GEL electrolyte is made up of a solution electrolyte "entrapped" inside molecular cages of PAN polymer, restricting the iodide ion mobility compared to a pure electrolyte solution or a nanofibre membrane soaked electrolyte solution. Further, The NFGEL electrolyte has a 3-dimensional network of nanofibres with much larger pore structure enabling high liquid like ionic mobility leading to high J_{sc} values and high efficiency compared to DSSC based on conventional GEL type electrolyte. Therefore, the overall performance of a DSSC with nanofibre membrane electrolyte is expected to be in between those of a pure electrolyte solution based DSSC and a conventional gel electrolyte based DSSC.

The DSSCs assembled with electrospun PAN nanofibre membrane gel electrolyte (NFGEL) exhibit a slightly lower short circuit current density (J_{sc}) and higher open circuit voltages (V_{OC}) than the liquid electrolyte (LEL) based DSSC (Table 1). The lower value of J_{sc} in the DSSC with NFGEL electrolyte may originate from its lower dye regeneration rate and lower iodide ionic conductivity as described earlier. Higher resistance for ion migration due to the presence of the nanofibre membrane host matrix reduces the iodide ion mobility and the lower dye regeneration rate limits the supply of I^-/I_3^- ions to shuttle between the TiO_2 electrode and the Pt counter electrode. This leads to a decrease in the J_{sc}. To substantiate this explanation, the interfacial charge transfer resistances of the three types of DSSCs were investigated by EIS measurements [19]. The Nyquist plots of the DSSCs with three different electrolyte systems are shown in Figure 5. The calculated values of the series resistance (R_S), charge transfer resistance of the Pt/electrolyte interface ($R1_{CT}$) and charge transfer resistance of the TiO_2/electrolyte interface ($R2_{CT}$) for the three types of DSSCs are tabulated in Table 2.

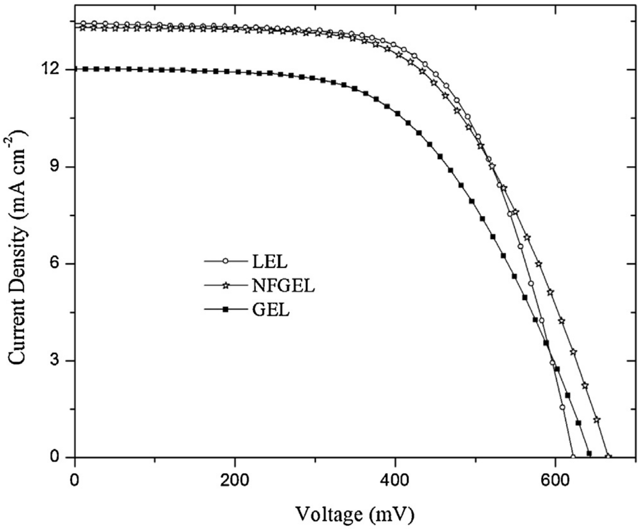

Fig. 4. Photocurrent-voltage curves for DSSCs with electrospun PAN nanofibre membrane gel electrolyte (NFGEL) with 9.14 μm thicknesses liquid electrolyte (LEL), and convenional PAN based gel electrolyte (GEL).

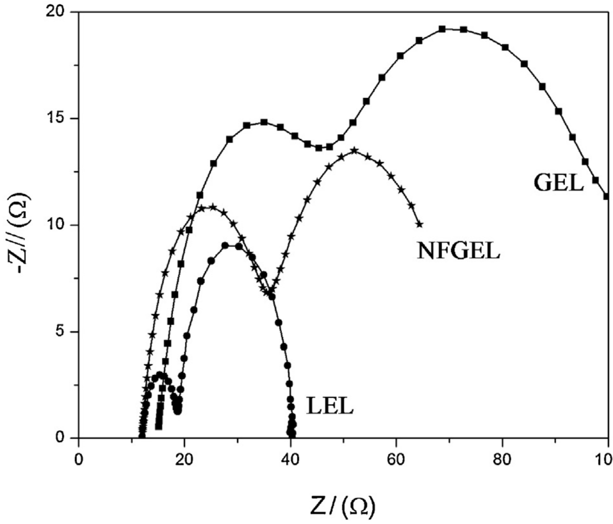

Fig. 5. Nyquist plots of the DSSC with configuration FTO/TiO_2/electrolyte/Pt/FTO using the PAN nanofibre membrane (9.14 μm thickness) gel electrolyte (NFGEL), liquid electrolyte (LEL) and gel electrolyte (GEL).

These results show that the series resistance as well as the charge transfer resistance values at the two electrode/electrolyte interfaces of the DSSC fabricated with NFGEL lie in between those of the LEL based DSSC and the GEL based DSSC. These results are consistent with the current densities of the three DSSCs listed in Table 1 and described earlier. As expected, the highest J_{sc} of the DSSCs corresponds to the devices with LEL electrolyte and the lowest J_{sc} to the cells with GEL, and the J_{sc} of the devices with NFGEL lies in between. The same explanation given earlier for the origin of the J_{sc} appears to be applicable here as well.

It is interesting to note that the product $J_{sc}R_s$ has values 160, 161 and 183 mV, respectively, for the DSSCs with LEL, NFGEL and GEL electrolytes. However, the DSSC with nanofibre membrane gel

Table 2
Series resistance (R_s), charge transfer resistance of the Pt/electrolyte ($R1_{CT}$), charge transfer resistance of the TiO_2/electrolyte ($R2_{CT}$) of DSSCs using the three different electrolytes.

	Liquid electrolyte (LEL)	PAN nanofiber membrane (9.14 μm) gel electrolyte (NFGEL)	PAN based gel electrolyte (GEL)
R_S (Ω)	11.89	12.10	15.22
$R1_{CT}$ (Ω)	07.65	23.81	30.51
$R2_{CT}$ (Ω)	20.81	28.36	46.18

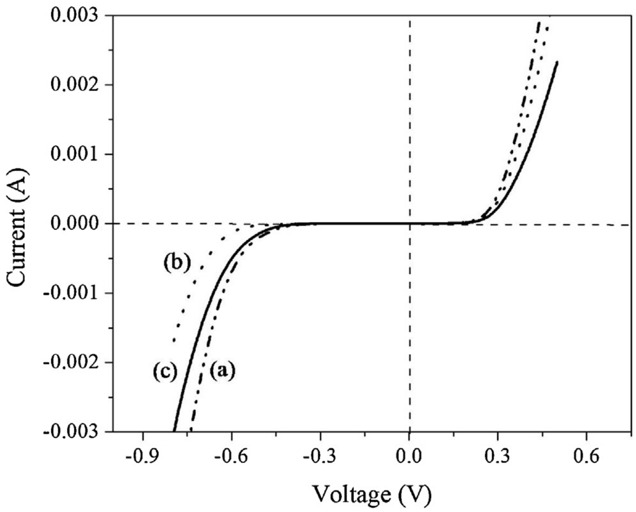

Fig. 6. Dark I-V characteristics of DSSCs with (a) liquid electrolyte (LEL) (b) electrospun PAN nanofiber membrane (9.14 μm thickness) gel electrolyte (NFGEL) and (c) PAN based conventional gel electrolyte (GEL).

electrolyte (NFGEL) exhibits a higher V_{oc} than the liquid electrolyte based cell. This could be due to the adsorption of the PAN nanofibre by the TiO_2 surface in contact with the nanofiber membrane, thereby causing a shift of the TiO_2 conduction band edge relative to the corresponding position in the liquid electrolyte based cell. One of the possible reasons for this might be due to the different band bending of the TiO_2 films as follows. As it is generally accepted, in the liquid electrolyte based cells, the adsorption of K^+ ions on the TiO_2 surface would cause a positively (downward) shift of the conduction band of TiO_2, thereby causing faster electron transfer dynamic at the TiO_2/dye interface resulting in enhanced J_{sc} at the expense of the V_{oc}. However in the NFGEL electrolytes based cells, the use of nanofiber matrix reduces both the ionic mobilities of I_3^-/I^- and K^+ caions due to the blocking effect compared to the liquid electrolyte cells. Therefore, the insertion of K^+ ions to the TiO_2 film would be lower than the liquid electrolyte cells, hence the positive shift of the conduction band of TiO_2 would be lesser than that in the liquid electrolyte cells, which eventually ending up with higher V_{oc} in NFGEL based devices. On the other hand in the GEL based cells the blocking effect is slightly lower than that in the NFGEL based devices due to the non existence of nano fibers. Therefore, the resulting effect in the band shift is also slightly lower than the NFGEL devices leading to an intermediate value for the V_{oc} in GEL based device.

To further support these explanations, dark I-V measurements were performed for the three different types of DSSCs studied in this work. The comparision of dark I-V characteristics for the DSSCs based on LEL, PAN nanofibre membrane based NFGEL electrolyte having thickness of 9.14 μm and conventional gel electrolyte (GEL) based DSSC are shown in Figure 6.

As it can be seen from the figure, the break down voltage at the negative region in the device comprising the NFGEL electrolyte is higher than that of the other two electrolyte based devices indicating that the electron recombination of the NFGEL based device is lower than the other two devices. Therefor, the rate of the reaction of I_3^- with electrons at the surface of the dyed TiO_2 electrode reduces leading to an increase in the V_{OC} value [10,14] and hence an enhanced efficiency very close to that of the DSSC with corresponding liquid electrolyte.

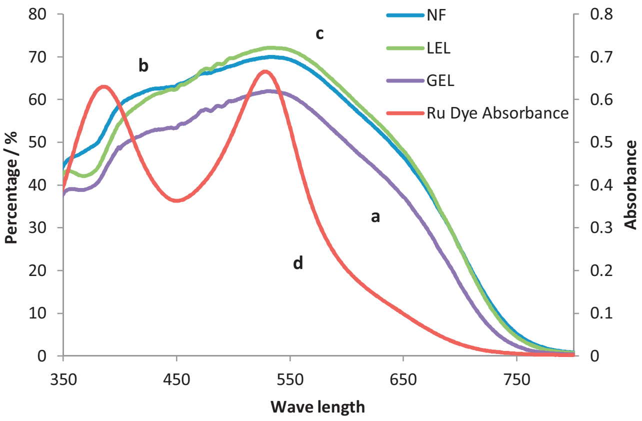

Fig. 7. Comparison of spectral responses (IPCE) of DSSCs with different electrolytes (a) GEL, (b) NFGEL and (c) LEL together with the absorption curve (d) of the Ru dye in ethanol.

Table 3
Correlation between V_{oc} and $J_{sc}R_s$ values for the DSSCs having the three different electrolytes.

	Liquid electrolyte (LEL)	PAN nanofiber membrane electrolyte (NFGEL)	PAN based gel electrolyte (GEL)
J_{sc} (mA cm^{-2})	13.42	13.31	12.03
V_{oc} (V)	0.62	0.67	0.64
R_s (Ohm)	11.89	12.10	15.22
$J_{sc}R_s$ (V cm^{-2})	159.56	161.0	183.1

The effectiveness of a cell to convert light of various wavelengths into electrical energy is measured by the incident monochromatic light current conversion efficiency (IPCE) defined as the number of electrons generated by light per number of photons incident on the cell given by the formula,

$$\mathrm{IPCE}\%(\lambda) = 1240(\mathrm{eV\,nm})J_{sc}(\mu\mathrm{A/cm}^2)/\lambda(\mathrm{nm})I(\mu\mathrm{W/cm}^{-2})$$

where λ is the wavelength of the absorbed photon and I is the light intensity at wavelength λ. IPCE measurements on the three DSSC systems were done under monochromatic light illuminations. Results are shown in Figure 7.

The UV-VIS absorption spectrum of the dye in ethanol (curve, d) and the IPCE measurements carried out on aforementioned solar cells employing different electrolytes but with similar TiO_2 electrodes are shown in Figure 7. The absorption curve (d) exhibits the usual intense absorption around 513 nm. As can be seen from the Fig. 7, while the DSSCs fabricated with liquid electrolyte LEL (curve c) showed the highest IPCE (Max IPCE 73% at 525 nm), DSSCs with GEL electrolyte (curve b) showed the lowest IPCE. Further, The DSSCs fabricated with NFGEL electrolyte (curve a) showed almost equal photoresponses but with slightly lower IPCE values compared to the DSSC made with liquid electrolyte LEL. However, all these three devices showed the IPCE performances mainly in the 350-600 nm range and the photocurrent action spectra resembled well with the absorption spectrum of the dye and the short circuit current densities depicted in the Table 1. Therefore, it is clear that, in these devices, the optical paths within the electrodes are not much affected by the nature of the electrolyte weather it is liquid, gel or the nanofibre gel.

Table 3.

4. Conclusions

In this work we have demonstrated that electrospun polymer nanofiber membranes of polyacrylonitrile (PAN) can be used as a nanofiber matrix to produce a nanofibre based polymer gel electrolyte by soaking the membrane in an electrolyte solution. The resulting nanofibre gel electrolyte (NFGEL) with optimum nanofibre film thickness of 9.14 μm has been used successfully as the electrolyte of a TiO_2 dye sensitized solar cell. The performance of the nanofibre gel electrolyte based DSSC is very close to the performance of a DSSC fabricated using a liquid electrolyte with similar composition but without the PAN polymer. DSSC with optimized nanofibre gel electrolyte showed the highest light-to-electricity conversion efficiency of 5.2% whereas an identical cell based on corresponding liquid electrolyte showed an efficiency of 5.3%. The open circuit voltage (V_{OC}), short circuit current density (J_{Sc}) and fill factor for the solar cell based on the NFGEL electrolyte was 0.67 V, 13.31 mA cm^{-2} and 59% respectively at an incident light intensity of 1000 W m^{-2} with a 1.5 AM filter. This suggests the possibility of using nanofibre-based gel electrolytes in the fabrication of DSSCs, instead of electrolyte solutions based on volatile organic solvents, thereby minimizing some of the major drawbacks currently encountered with DSSCs made with solution electrolytes and at the same time obtaining efficiencies comparable to those with solution electrolyte based DSSCs.

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