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Performance of dye sensitized solar cells fabricated with electrospun polymer nanofiber based electrolyte

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Abstract

Nanofiber (NF) based gel polymer electrolytes were prepared by soaking electrospun polyacrylonitrile (PAN) nanofiber membranes of different thicknesses in an optimized liquid electrolyte having the composition of 0.8 g PC: 0.17 g $Pr_4NI : 0.0139$ g I_2 . Dye Sensitized Solar Cells (DSSCs) of configuration FTO/TiO₂/dye/PAN NF:Pr₄NI:PC:I₂/Pt/FTO were fabricated using gel electrolyte films of different thicknesses and characterized using *I-V* measurements. The DSSC fabricated with the gel electrolyte with optimized nanofiber membrane thickness showed an efficiency of 5.44% with an open circuit voltage of 735.0 mV, short circuit current density of 14.49 mA cm⁻² and a fill factor of 51.06%.

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1. Introduction

Dye sensitized solar cells (DSSCs) are widely recognized as a contemporary technology to harvest the sunlight with economically viable cost owing to their simple fabrication procedure and benign effects on the environment [1.2,3]. The performance of a dye sensitized solar cell varies depending on the composition and the physical state of the electrolyte [4]. Even though the liquid electrolyte based DSSCs have shown the highest efficiencies around 11% (maximum for DSSCs that is related with our projects using iodide ion conducting electrolyte) so far, its lack of long term stability due to sealing problems, leakage of solvent, photodecomposition of the dye in the solvent medium due to usage of volatile liquids, electrode corrosion, and flammability have prevented large scale practical applications of DSSCs [4,5,6]. Consequently, replacement of the liquid electrolytes by solid state electrolytes and quasi-solid state (or gel) electrolytes have been extensively studied over the past many years with a view to eliminate most of the above mentioned disadvantages found in liquid electrolyte based DSSCs [4]. However, due to poor physical contact at TiO₂/dye/solid electrolyte interface, the efficiencies of solid state electrolyte based DSSCs were found to be significantly lower than that of liquid electrolyte based cells, hindering practical applications [4]. Many problems associated with both liquid and solid state electrolytes can be overcome by using a new type of hybrid electrolyte known as quasi-solid state or gel electrolyte and DSSCs based on these have better long term stability than liquid electrolytes and also high ionic conductivity and outstanding interfacial contacts than solid state electrolyte based cells. Moreover, their nonflammable nature, negligible vapor pressure, good permeability into mesoporous TiO_2 are advantages over all the other types of electrolytes studied so far. Owing to these benefits quasi-solid state (gel) electrolytes, have received a considerable attention in the recent past in the field of DSSCs [4].

One of the methods to realize a quasi-solid state or gel electrolyte is by incorporating a liquid electrolyte within a suitable polymer where the polymer matrix acts as a host to trap the liquid electrolyte. Although DSSCs composed of these polymer gel electrolytes do not suffer from problems such as the loss due to evaporation of the electrolyte solution, they still have relatively low light-to-electricity conversion efficiencies because of the lower electron injection and lower ionic conduction within the electrolyte material [4]. As a result of intensive research on nano materials during the last two decades, now it is possible to produce a novel quasi-solid state (gel) electrolyte by incorporating a solution electrolyte within a nanofiber membrane matrix [7]. Owing to their high porosity with excellent pore interconnectivity and extremely high specific surface area due to their small diameter, nanofibers have been recognized as one of the most attractive nanostructures [8]. Polymeric nanofibers can be fabricated using several different methods such as self-assembly, template synthesis, drawing, phase separation, melt blowing, solvent casting and electrospinning. Among these, electrospinning appears to be one of the most convenient and cost effective methods considering the fact that it can fabricate long and continuous nanofibers with adjustable diameters [7,8,9].

The properties of the polymer solution out of which polymer nanofibers are drawn, have the most significant influence in the electrospinning process and the resultant fiber morphology. Polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyvinylidene fluoride-cohexafluoropropylene (PVDF-HFP) are particularly suitable for fabricating polymer nanofiber membranes as host matrices for gel electrolytes [9,10]. Polyacrylonitrile (PAN) is a well-known polymer having excellent characteristics such as electro-spinnability, environmental benign nature, good stability, favorable mechanical properties and commercial viability [10]. In this work, an electrospun PAN nanofiber membrane matrix activated by a liquid electrolyte has been successfully used to fabricate a quasi-solid (gel) electrolyte to enhance the light harvesting efficiency in the DSSCs.

2. Experimental

2.1. Materials

Commercial grade P-25 TiO₂ nano particles purchased from Degussa, Fluorine doped SnO₂ (FTO) layered glass (Nippon sheet resistance 15 Ω /sq), Ruthenium dye (N 719) purchased from Solarnix SA, Triton X-100, Acetic acid, Ethanol, Propylene Carbonate (PC), Tetra propyl ammonium iodide (Pr₄N⁺Γ), Iodine (I₂) with purity>98%, Polyacrylonitrile (PAN- Avg. Mw 150,000) and N,N-dimethylformamide (DMF) purchased from Sigma Aldrich were used as starting materials.

The photoanode was initially prepared with TiO_2 paste by mixing 0.20 g of P-25 TiO_2 powder with 12 drops (0.15 g) of Acetic acid, one drop (0.02 g) of Triton X-100, about 2 ml of ethanol and doctor blading it on the conducting side of a pre-cleaned fluorine doped Tin Oxide (FTO) glass such that the effective area of the cell was 0.25 cm². After the sintering process, TiO_2 film was allowed to cool down to room temperature and was immersed in an ethanolic dye solution containing Ruthenium dye N719 (0.3 mM) for 24 hours for dye absorption [11]. For the liquid electrolyte, propylene carbonate (PC) and tetrapropyle ammonium iodide salt (Pr_4NI) were mixed with different weight ratios (keeping the PC weight 0.80 g and varying Pr_4NI weight). Then appropriate amount of I₂ for each sample (1:10 molar ratio) was added to the above mixture and the solution was stirred using a magnetic stirrer for 24 hours.

S.S. Dissanayake et al. / Materials Today: Proceedings 3S (2016) S104 – S111

The electrospun PAN nanofiber membranes were prepared using the NABOND electrospinning system (NaBond Technologies, Hong Kong). The solution used to produce nanofibers was prepared from 11% WW solution of PAN in DMF. The mixture was first heated at 140 $^{\circ}$ C with constant stirring until a transparent homogeneous polymer solution was formed [7]. Then it was allowed to cool down to room temperature and was transferred to a syringe pump connected to a stainless steel needle and the flow rate was adjusted to 2 ml/h. A high voltage of 8 kV was applied between the tip of the needle and the grounded drum collector which were fixed to be 6.5 cm apart. The PAN nanofibers were deposited on to polished platinum plates which were attached to the drum collector by an aluminium foil. The drum was adjusted to rotate with a rotational speed of 810 rpm. In order to vary the thickness of the nanofiber membrane, the electrospinning time was altered. Fig. 1 shows the electrospinning apparatus used to form PAN nanofiber membranes.

The nanofiber membrane deposited on platinum plate which was attached to the aluminium foil was carefully removed from it and about three drops of the liquid electrolyte just sufficient to swell the nanofiber membrane mat was spread on the nanofiber mat and kept for about an hour to form the quasi-solid state nanofiber electrolyte. The excess liquid was carefully wiped off. The DSSC was fabricated by sandwiching the above gel electrolyte film in between the Pt plate counter electrode and TiO_2 coated FTO glass photo anode.



Fig. 1. The electrospinning system used for the fabrication of PAN nanofiber membranes.

2.3. Characterization of the electrolyte and dye sensitized solar cells

DC polarization test was conducted for the liquid electrolyte samples sandwiched between two polished stainless steel (SS) electrodes, with the configuration SS/Electrolyte/SS using the Metrohm Autolab PGSTAT128N with an applied DC potential of 0.5 V [12]. Complex impedance measurements were carried out to study the conductivity by using Metrohm Autolab PGSTAT128N with FRA32 in the frequency range 0.01 Hz – 1 MHz using stainless steel (SS) electrodes with configuration SS/Electrolyte/SS [13]. The current-voltage (*I-V*) characteristics of the DSSCs fabricated with the liquid electrolytes and the nanofiber membrane (gel) electrolytes were measured under the illumination of 100 mW cm⁻² (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 multimeter with potentiostat/galvonostat HA-301.

3. Results and Discussion

3.1. DC polarization test for liquid electrolytes

Results of the Wagner's DC polarization test for the SS/electrolyte/SS symmetrical cell, plotted as current/initial current versus time is shown in figure 2.



Fig. 2. Graph of current/initial current versus time for the liquid electrolyte with composition 0.8 g PC, 0.17 g Pr₄NI, 0.0139 g I₂.

The electronic transference number estimated from the DC polarization test data is around 0.05. The electronic transference numbers for all the electrolyte samples were close to zero indicating that the electronic conductivity in these samples is negligible and the electrolyte samples are predominately ionic conductors.

3.2. Ionic conductivity of liquid electrolytes

The ionic conductivity values of the liquid electrolyte samples with different Pr_4NI salt content were calculated using the resistance values extracted from complex impedance measurements. Figure 3 shows the ionic conductivity of the liquid electrolyte samples as a function of the Pr_4NI salt concentration.

According to the conductivity vs salt concentration plot, with increasing salt concentration, the conductivity of the liquid electrolyte continuously increases and the salt is completely soluble in the electrolyte solution. When the concentration of Pr_4NI increases, the I concentration also increases as expected due to the ionic dissociation of the salt, resulting an increase in the ionic conductivity as seen in Fig.3.

However, after a certain salt concentration, around 0.17 g (in 0.8 g of PC), the solution gets saturated with the salt, making the salt insoluble any further and the salt solubility limit has been reached.

In the salt insoluble region, due to the presence of undissolved Pr_4NI salutes and added I_2 in the 1:10 molar ratio, it is possible to form ionic aggregates such as (Pr_4NI_2). These can make an additional contribution to the ionic

conductivity of the medium even beyond the solubility limit. This is very likely the reason for a little higher ionic conductivity beyond the solubility limit.



Fig. 3. Conductivity of the liquid electrolyte (Pr₄NI in PC) versus the weight of the Pr4NI salt dissolved in a 0.8 g of PC.

The liquid electrolyte with the maximum salt concentration in the solubitily limit (0.17 g in 0.8 g of PC) was taken as the optimized liquid electrolyte to be incorporated into the electrospun nanofiber matrix.

3.3. I-V characteristics of DSSCs based on the liquid electrolyte

The *I-V* characteristics of DSSCs based on the liquid electrolyte samples with different Pr_4NI weight ratios were measured under the illumination of simulated sunlight. From repeated measurements for several cells with the same electrolyte composition, the best efficiency cell was selected and the variation of efficiency with the salt weight ratio is shown in figure 4.



Fig. 4. DSSC efficiency based on liquid electrolyte versus the weight of the salt dissolved.

According to the efficiency vs salt concentration plot, the efficiency increases up to the salt solubility limit of the corresponding liquid electrolyte and then decreases. A comparison of Fig. 3 and 4 suggests that the efficiency of the liquid electrolyte based DSSC is essentially determined by the ionic conductivity of the liquid electrolyte which is largely determined by the mobile iodide ion (I) concentration [11]. In the electrolyte, iodide ion conductivity contribution is expected to be much more dominant, compared to the contribution from the bulky and less mobile Pr_3N^+ ions.

Even though the overall ionic conductivity has increased with Pr_4NI content, and also the iodide ion concentration has increased with Pr_4NI content, the iodide ion conductivity has gone through a maximum and reaches a constant value, which corresponds to the Jsc maximum. The remaining excess iodide ions, (beyond the maximum efficiency composition) remain in the medium as higher ionic clusters without contributing to the Jsc.

The optimum liquid electrolyte composition to fabricate the nanofiber membrane based electrolyte was taken as the composition with 0.17 g Pr_4NI in 0.8 g PC with 0.0139 g I_2 . The *I-V* characteristics of the optimized DSSC based on this liquid electrolyte had an efficiency of 5. 84%, an open circuit voltage of 758.0 mV, short circuit current density of 12.86 mA cm⁻² and a fill factor of 59.87%.

3.4. I-V characteristics of DSSCs based on PAN nanofiber membrane based gel electrolyte

The liquid electrolyte with the composition of 0.17 g Pr_4NI , 0.8 g PC and 0.0139 g I_2 was used to swell the PAN nanofiber mat and the *I-V* characteristics of DSSCs fabricated with nanofiber membrane electrolyte having the configuration FTO/TiO₂/dye/PAN NF:Pr₄NI:PC:I₂/Pt/FTO were measured under the illumination of 1000 mW cm⁻² simulated sunlight. The efficiencies of DSSCs with nanofiber membrane electrolytes showed dependence on the electrospinning time (corresponding to the nanofiber thickness) as shown in figure 5. Several numbers of solar cells were measured to make sure that the efficiency values are repeatable.



Fig. 5. Variation of efficiency of nanofiber gel electrolyte based DSSCs with electrospinning time for PAN nanofiber membrane. For each electrospinning time used for the electrospun nanofibers used in the gel electrolyte, several DSSCs were fabricated and tested. These data points are shown in the figure.

This shows that, the thickness of the nanofiber mat directly affects the efficiency of the solar cell. The maximum efficiency was observed for the thickness which corresponds to the electrospinning time of 1 minute [11,14]. The optimized DSSC fabricated with this nanofiber membrane electrolyte showed an efficiency of 5.44%, J_{sc} of 14.49 mA cm⁻², V_{oc} of 735 mV and fill factor of 51.06%. These values are only slightly less than the corresponding quantities for the liquid electrolyte based cells described earlier. A comparison of the *I-V* characteristics of DSSCs with liquid electrolyte and PAN nanofiber electrolyte is shown in figure 6.



Fig. 6. I-V characteristics curves for DSSCs with liquid electrolyte and electrospun PAN nanofiber membrane (gel) electrolyte.

As seen from Fig.5, the variation of efficiency with the thickness of the nanofiber membrane is directly related to the iodide ion conductivity in the electrolyte medium up to a certain thickness of the nanofiber mat (correspond to a electrospinning time of 1 min.). When the thickness of the nanofiber membrane is small (smaller electrospinning times), the number of pores in the membrane is low and consequently the amount of liquid electrolyte that the membrane can uptake is also low. Hence the amount of electrolyte per unit volume is low and the electrolyte/Dye TiO₂ contact area is also low. Both these contribute to low efficiency. When the thickness of the nanofiber mat is increased up to the optimum value (1 min electrospinning time), the number density of nanofibers and the volume of pore space increase providing more volume for electrolyte uptake. Reduced electron recombination, compared to the liquid electrolyte based DSSC appears to be the very likely mechanism for the improved J_{sc} in the nanofiber based DSSC. When the nanofiber membrane thickness increases beyond this optimum value (electrospinning time longer than 1 min.), the number of cross linking points also increases limiting the available pore space combined with higher mechanical strength. As a result, the resulting nanofiber matrix becomes more rigid and more dense and the blocking effect due to too many fibres and too many cross linking centres reduces the iodide ion mobility and therefore reduces the J_{sc} and the efficiency [7,15,16].

4. Conclusions

From the *I-V* characteristics for the DSSCs based on liquid electrolyte, it can be seen that the solar cell efficiency maximum was obtained for the composition of 0.17 g of Pr_4NI in 0.8 g of PC which was also the maximum Pr_4NI salt concentration obtained within the solubility limit.

The *I-V* characteristics of DSSCs fabricated with electrospun nanofiber membrane (gel) electrolyte show that the parameters of the DSSCs varies with the thickness (electrospinning time) of the nanofiber membrane. Hence it can

be suggested that the variation of efficiency with the thickness of the nanofiber membrane electrolyte is directly related to the iodide ion conductivity in the electrolyte medium. For the DSSC based on PAN nanofiber membrane electrolyte of optimized thickness (1 min electrospinning time) having the same optimized salt concentration as the liquid electrolyte, the maximum efficiency of 5.44% was obtained.

The best efficiency of the DSSC with nanofiber membrane based electrolyte is very close to the best efficiency of the liquid electrolyte based DSSC. Hence it can be concluded that the nanofiber membrane based electrolyte is one of the best alternatives to overcome many of the drawbacks associated with liquid and solid-state electrolytes based DSSCs.

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