Electrochimica Acta 266 (2018) 276-283

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Contents lists available at ScienceDirect

# Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Characterization of poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) nanofiber membrane based quasi solid electrolytes and their application in a dye sensitized solar cell



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#### ARTICLE INFO

Article history: Received 22 November 2017 Received in revised form 4 February 2018 Accepted 4 February 2018 Available online 6 February 2018

Keywords: Dye sensitized solar cells PVdF-HFP co-polymer Nanofiber Gel polymer electrolyte FTIR spectroscopy

# ABSTRACT

The electrolyte plays a major role in dye sensitized solar cells (DSSCs). In this work a quasi-solid state (gel) electrolyte has been formed by incorporating a liquid electrolyte made with KI dissolved in ethylene carbonate (EC) and propylene carbonate (PC) co-solvent in poly (vinylidene fluoridehexafluoropropylene) (PVdF-HFP) co-polymer nanofiber membrane prepared by electrospinning. SEM images of the electrolyte membrane showed the formation of a three-dimensional network of polymer nanofibers with diameters between 100 and 300 nm and an average membrane thickness of  $14 \,\mu$ m. The electrolyte was characterized by FTIR and differential scanning calorimetry (DSC) measurements. The DSSCs fabricated with this electrolyte were characterized by current-voltage and Electrochemical Impedance Spectroscopy (EIS) measurements. DSC thermograms revealed that the crystallinity of the PVdF-HFP nanofiber is 14% lower than that of the pure PVdF-HFP polymer while the FTIR spectra showed a reduced polymer-polymer interaction in the nano fiber based gel electrolyte. The DSSCs fabricated with nanofiber based gel electrolyte showed an energy conversion efficiency of 5.36% under 1.5 a.m. solar irradiation, whereas the efficiency of the DSSC made with the liquid electrolyte based cell was 6.01%. This shows the possibility of replacing the liquid electrolyte in DSSCs by electro-spun polymer nanofiber based gel electrolyte and thereby minimizing some major drawbacks associated with liquid electrolyte based solar cells while maintaining a reasonably high efficiency.

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#### 1. Introduction

Today, energy has become a key driving force of day-to-day lives of people and economic growth of a country [1]. Solar energy has the potential to meet a substantial part of our future energy demand [2]. A majority of the commercial photovoltaic devices that are available today are based on silicon. However, in recent time dye sensitized solar cells (DSSCs) have gained much attention due to the simple and low cost cell fabrication process compared to conventional silicon solar cells. Most of the DSSCs are primarily composed of a nano-crystalline titanium dioxide (TiO<sub>2</sub>) photoanode sensitized by a dye which acts as the photosensitizer, a counter electrode and an electrolyte separating the two electrodes. In a DSSC photo-excitation occurs at the dye adsorbed on to TiO<sub>2</sub> and photo-generated electrons are injected into the conduction band of the semiconducting TiO<sub>2</sub> layer. The oxidized photosensitizing dye is regenerated by redox reactions taking place at the interfaces facilitated by the electrons transferred by the external circuit to the counter electrode [3].

Many studies have been conducted to replace the liquid

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electrolyte used in DSSCs by a quasi-solid state (gel) electrolyte in order to overcome durability and stability issues caused by liquid volatility, leakage and dye desorption [4–6]. Gel electrolytes reduce the risk for internal shortening and leakage issues and are more suitable for commercial production [7,8]. Another recent development for DSSC electrolytes is to use quasi solid (gel) electrolytes made by soaking a polymer nano fiber membrane in a solution electrolyte [9]. These gel electrolytes with a structured network of polymer nanofibers exhibit ionic conductivity values close to those of a liquid electrolyte but maintain a quasi-solid structure thereby reducing solvent evaporation and leakage and providing mechanical stability. In addition, since the nano-fiber membrane acts as a separator the fabrication of this kind of cells is relatively easy [10].

There are several methods to produce polymer nano-fibers such as electrospinning, template methods, vapor growth, and phase separation [11-13]. Out of these, the electrospinning method which has been known for more than a century, has become popular for the production of polymer nanofibers for various applications [14-16].

In this study we have used the co-polymer poly-(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), because when it is in the gel state it shows a low glass transition temperature, high solubility for organic solvents and low crystallinity [17,18]. Accordingly, there are more amorphous domains in PVDF-HFP which could absorb large amounts of liquid electrolytes and gain sufficient mechanical integrity to produce a free-standing electrolyte membrane. PVdF-HFP polymer nanofiber membranes with different thicknesses were produced by electrospinning and used to prepare nanofiber gel electrolytes. Ion/polymer/solvent interactions of the polymer nanofiber gel electrolytes were investigated using Fourier Transform Infrared spectroscopy (FTIR) while thermal transitions were studied using Differential Scanning Calorimetry (DSC). DSSCs were fabricated under identical conditions with (a) a liquid electrolyte, (b) a polymer nanofiber gel electrolyte, and (c) a conventional gel electrolyte and their performances were compared. The interfacial charge transfer resistances of the three different types of DSSCs were investigated by electrochemical impedance spectroscopy measurements (EIS).

## 2. Experimental

## 2.1. Materials

Ethylene carbonate (EC), propylene carbonate (PC), iodine chips (I<sub>2</sub>) and KI with purity greater than 98% were purchased from Fluka. PVdF-HFP pellets (Mw ~ 400,000) were purchased from Sigma Aldrich. Ruthenizer 535-bisTBA (N719) sensitizer dye and fluorine doped SnO<sub>2</sub> coated (FTO) glass (sheet resistance 12  $\Omega$ /sq) was purchased from Solaronix SA.

# 2.2. Preparation of the PVdF-HFP nanofiber membranes

PVdF-HFP nano fibers were prepared using a Nabond electrospinning system (NaBond Technologies, Hong Kong). The electrospinning solution was prepared by dissolving PVdF-HFP pellets (1.0 g) in 9.0 ml of DMF (Sigma Aldrich) and stirring overnight to form a transparent homogenous solution. A 10 kV DC voltage was applied between the spinneret and the drum collector and the syringe pump flow rate was adjusted to 1 ml h<sup>-1</sup>. The electro-spun PVdF-HFP nano fibers were collected onto platinized glass plates attached to the drum collector for about 3 min. For SEM measurements the electro-spun PVdF-HFP nano fibers were collected onto FTO glass plates. The rotational speed of the drum collector during nanofibre deposition was 825 rpm and the distance between the collector and the syringe tip was 6.5 cm.

#### 2.3. Fabrication of the DSSC's

The first colloidal suspension was prepared by grinding together 0.25 g of TiO<sub>2</sub> (Evonic P90 Aeroxide) and 0.1 M HNO<sub>3</sub> A compact layer of TiO<sub>2</sub> of fine particles of size ~14 nm was deposited on precleaned fluorine doped tin oxide (FTO) glass plate (Nippon sheet glass  $10-12 \Omega/sq$ ) by spin coating the suspension at 3000 rpm. sintering it at 450 °C for 45 min and by slowly cooling it down to ambient temperature. The size of the FTO glass plate was ~1 cm  $\times$  0.5 cm and a half of the FTO plate was covered by a peace of scotch tape to prevent coating TiO<sub>2</sub> on the area needed for the electrical contact. Therefore, TiO2 coated area of the cell was ~0.5 cm  $\times$  0.5 cm. Another TiO<sub>2</sub> colloidal suspension was prepared by mixing 0.25 g of TiO<sub>2</sub> (Degussa P-25), 0.1 M nitric acid, 0.02 g triton X-100 and 0.05 g PEG 1000 (Fluka) and the resulting paste was spread over the first TiO<sub>2</sub> compact layer by doctor blade technique to obtain a photoanode with larger particle size (~21 nm) and an active cell area of 0.25 cm<sup>2</sup> was used. The resulting two layer TiO<sub>2</sub> photoanode was finally sintered again at 450 °C and allowed to cool back to room temperature. These electrodes were then immersed in an ethanolic (Di-tetrabutylammonium cis-bis(isothiocyanato)bis (2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium (II)) dye solution for 24 h for dye absorption in order to prepare the dye sensitized TiO<sub>2</sub> photo-anode.

The electrolyte solution was prepared by dissolving 0.06 g of KI and 9.2 mg of I<sub>2</sub> in an EC (0.4 g) and PC (0.4 g) mixture. Few drops of the liquid electrolyte were carefully placed on the nanofiber membrane deposited platinum plate and kept for about 1 h for the absorption of the electrolyte solution by the nanofiber matrix to form a quasi-solid-state (or gel) electrolyte. The excess electrolyte was carefully wiped off to make sure that no free electrolyte solution was left on the platinized counter electrode. Dye sensitized solar cells were fabricated in the configuration FTO/TiO<sub>2</sub>/electrospun nanofiber membrane gel electrolyte/Pt/FTO with an active cell area of 0.25 cm<sup>2</sup>. For comparing the device performance two other types of DSSC's were also fabricated, one with the liquid (solution) electrolyte and the other with a conventional gel electrolyte with PVdF-HFP co-polymer.

The liquid electrolyte was prepared using the same composition given above and the conventional gel polymer electrolyte samples were prepared by using the weights of PVdF-HFP (0.1 g), EC (0.40 g) PC (0.40 g) KI (0.06) and iodine (0.009). The relevant weights of EC, PC, Pr<sub>4</sub>NI and KI were mixed in a closed glass bottle by continuous stirring at room temperature for a few hours. Subsequently, PVdF-HFP was added to the above mixture and heated to about 125 °C for a few minutes until a transparent slurry was obtained. After the mixture was cooled down to about 50 °C, I<sub>2</sub> chips were added and the mixture was continuously stirred for about an hour to get the conventional gel polymer electrolyte.

#### 2.4. Measurements

The morphology of the electro-spun polymer nanofiber membranes were observed by Scanning Electron Microscopy (SEM; HITACHI-SU8220). The thicknesses of the membranes were determined from the SEM images of their cross sections. The current density versus cell potential (*J-V*) characteristics of the DSSCs having an active cell area about ~0.25 cm<sup>2</sup> were measured using a computer-controlled Keithley 2000 multimeter with Potentiostat/ Galvanostat HA-301 under the illumination of 1000 W m<sup>-2</sup> using a Xenon 500 lamp with an AM 1.5 filter. Electrochemical Impedance Spectroscopy (EIS) measurements were performed on the DSSCs using a 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 also carried out under the illumination of  $1000 \text{ Wm}^{-2}$  using the same solar simulator. Differential Scanning Calorimetry (DSC) thermograms were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter. Each sample was scanned between -70 and  $170^{\circ}$ C at a heating rate of 10  $^{\circ}$ C per minute. The FTIR spectra for the samples were obtained in the attenuated total reflectance (ATR) mode at room temperature using a Bruker Alpha FTIR spectrometer with a *Platinum ATR* (Ge crystal) module and a spectrometer in the range 400–4000 cm<sup>-1</sup> with 1 cm<sup>-1</sup> resolution.

# 3. Results and discussion

# 3.1. Morphological and photovoltaic studies

Fig. 1 shows the SEM images of the electro-spun PVdF-HFP nanofiber membrane. It is known that the applied voltage, tip to collector distance (TCD) and polymer concentration are the main parameters of the electro-spinning method that govern the surface morphology and fiber diameter of the resulting nano fiber membrane [9]. The membrane used for the highest efficiency solar cell has a thickness of about 14 µm and consists of a three-dimensional network of polymer nanofibers with diameters between 100 and 300 nm, see Fig. 1. This three-dimensional network is highly porous and interconnected. The cross linking of the nano fiber network, as seen from Fig. 1, improves the mechanical strength and stability of the membrane. The highly porous morphology facilitates the more liquid electrolyte uptake and retention forming the quasi-solid state or gel electrolyte with ionic conductivity values close to those of the corresponding liquid electrolyte while maintaining the advantages of a quasi-solid state (non-flowing gel). Since the polymer nanofibres were deposited on FTO glass for the SEM study, the small grains underneath the polymer nanofiber seen in Fig. 1-(a) are tin oxide crystallites on the FTO glass.

The *J*-*V* curves of the DSSCs fabricated with quasi-solid-state nanofiber electrolyte, conventional gel electrolyte and corresponding liquid electrolyte are shown in Fig. 2. The cell parameters such as the open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (*FF*) and efficiency ( $\eta$ ) were calculated using these *J*-*V* curves.

The corresponding photovoltaic parameters are given in Table 1. The highest  $J_{sc}$  was observed for the DSSC with the liquid electrolyte as expected. This is evidently due to the higher ionic conductivity of the liquid electrolyte compared to the other two electrolytes. The lowest  $J_{sc}$  is shown by the cell with a conventional gel electrolyte. It can be explained by that the PVdF-HFP and PC based conventional gel electrolyte behaves as a uniform, viscous medium formed by the gelation whereas for the nanofiber based gel electrolyte, the liquid



Fig. 2. Photocurrent-voltage curves for DSSCs with PVdF-HFP nanofiber membrane gel electrolyte (14.3  $\mu$ m thickness), liquid electrolyte and conventional gel electrolyte.

#### Table 1

Photovoltaic parameters of the DSSCs based on conventional liquid electrolyte, polymer nanofiber quasi solid state electrolyte and conventional polymer gel electrolyte having the same compositions.

Electrolyte	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{\rm mV}$	FF/%	η/%
Liquid Nano fiber gel Conventional gel	$\begin{array}{c} 13.5 \pm 0.5 \\ 11.8 \pm 0.5 \\ 10.1 \pm 0.3 \end{array}$	$681 \pm 11$ $694 \pm 13$ $710 \pm 12$	$65.5 \pm 1.5$ $65.3 \pm 1.9$ $65.6 \pm 0.9$	$\begin{array}{c} 6.0 \pm 0.1 \\ 5.4 \pm 0.2 \\ 4.7 \pm 0.2 \end{array}$

electrolyte is "trapped" and retained within the cages formed by the 3D network of the polymer nanofiber membrane structure while facilitating the "almost liquid like" ionic transport through the interconnected pore-structure. Conductivity values and therefore photocurrent densities close to those of the liquid electrolyte based cells are consequently obtained.

As seen in Table 1, an opposite trend is observed for the  $V_{oc}$  and also for the cell potential at low current densities shown in Fig. 2. For a typical DSSC under illumination,  $V_{oc}$  is defined as the difference between the Fermi level of the TiO<sub>2</sub> semiconductor and the redox level of the electrolyte under open circuit. This difference is created by the photo-generated electrons in the TiO<sub>2</sub> conduction band. If the ionic conductivity of the electrolyte is high, the rate of transport of photo-generated electrons from the TiO<sub>2</sub> through the external circuit to the counter electrode and then to the electrolyte



Fig. 1. SEM images of the electro-spun PVdF-HFP membrane deposited on FTO glass, (a) top view and (b) cross section view of the membrane.

and the dye is higher. In addition charge transport in the bulk and at the interfaces is high for the liquid electrolyte (shown by EIS measurements). Therefore, the difference between the Fermi level and the redox level is lower for cells with a high conducting electrolyte since faster charge transport leads to a reduction in the number of photo-generated electrons in the conduction band [10]. When the circuit is open, conduction band electrons recombine with the ions in the electrolyte and with holes in the valence band. Faster the charge transfer kinetics, higher is the recombination rate at the open circuit. The difference between the Fermi level and redox level at the equilibrium defines the  $V_{\rm oc}$  of the cell. Therefore, the highest cell potential at low current densities is obtained for the gel electrolyte based cell due to the slow recombination kinetics while the lowest cell potential at low current densities is found for the liquid electrolyte based cell due to faster recombination, see Fig. 2. The fill factor FF remains almost the same for all the DSSCs. This can possibly be due to the use of similar photo electrodes in the cells [19,20].

The efficiencies of the DSSCs fabricated with liquid electrolyte, PVdF-HFP nano fiber membrane based quasi solid state (gel) electrolyte and conventional gel electrolyte were 6.01, 5.36 and 4.70% respectively. These results show that the DSSC based on electrospun PVdF-HFP nanofiber gel electrolyte has a 14% efficiency enhancement compared to the DSSC that used a conventional gel electrolyte.

#### 3.2. Electrochemical impedance spectra

Electrochemical impedance spectroscopy (EIS) was used to investigate the interfacial resistances of the DSSC's which influence the net ionic conductivity and finally affect the  $J_{sc}$ . Nyquist plots of the three types of DSSCs with configuration FTO/TiO<sub>2</sub>/electrolyte/ Pt/FTO are shown in Fig. 3. The inset in Fig. 3 shows the equivalent circuit used to fit the EIS data. Parameters  $R_s$ ,  $R_{1CT}$ , and  $R_{2CT}$  are defined as the series resistance, the charge transfer resistance of the Pt/electrolyte interface, and the charge transfer resistance of the TiO<sub>2</sub>/electrolyte interface respectively [9,21,22]. Curves in Fig. 3 were used to calculate the charge transfer resistances given in Table 2. According to the data, the series resistance and interfacial charge transport resistances ( $R_s$ ,  $R_{1CT}$ , and  $R_{2CT}$ ) are the lowest for the DSSC fabricated with liquid electrolyte [23,24]. Therefore, the



Fig. 3. Electrochemical Impedance Spectra of the DSSCs made with different electrolytes. Inset: The equivalent circuit of the device.

Table 2

Impedance parameter	s of DSSCs	with different	electrolytes.
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DSSC Electrolyte	$R_s/\Omega$	$R_{\rm CT1}/\Omega$	$R_{\rm CT2}/\Omega$	τ/ms	η/%
Liquid Nano Gel	$\begin{array}{c} 10.5 \pm 0.5 \\ 11.2 \pm 0.5 \\ 12.4 \pm 0.3 \end{array}$	$\begin{array}{c} 3.0 \pm 0.9 \\ 3.1 \pm 1.0 \\ 9.4 \pm 1.2 \end{array}$	$17.9 \pm 1.6$ $18.1 \pm 1.7$ $28.5 \pm 1.4$	7.54 8.37 8.87	6.01 5.36 4.70

highest charge transport at the interfaces and in the bulk is shown by the liquid electrolyte based cells. The observed highest  $J_{sc}$  in these cells thus depends on the higher charge transport at both interfaces and in the bulk. Conversely, the DSSC with conventional gel polymer electrolyte exhibits the highest resistance values in the bulk as well as at the interfaces. Nanofiber electrolyte based cells exhibit intermediate charge transport resistances. The trend of the variation of charge transport resistances in the bulk and at the interfaces correlate with the variation of the  $J_{sc}$  values. As already discussed the liquid electrolyte based cells exhibit higher short circuit current density and efficiency values but their practical applications are limited due to stability issues associated with volatility of solvents [4-7]. Therefore, PVdF-HFP nano-fiber based quasi solid state solar cells that exhibit 5.36% energy conversion efficiency and  $11.82 \text{ mA cm}^{-2} J_{sc}$  provides a better compromise for practical applications of DSSCs.

In order to understand the charge transport kinetics in the three different types of DSSCs Bode phase diagrams were used to estimate the lifetime of electrons within the TiO<sub>2</sub> photo-anode. The electron lifetime,  $\tau_{\rm p}$  is determined from the peak in the mid frequency range of the phase angle versus frequency plot [9,25,26],

$$\tau_r = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \tag{1}$$

where  $\omega_{\text{max}}$  and  $f_{\text{max}}$  are the angular frequency and the frequency of that peak. This  $\tau_r$  value is related to the charge transfer at the TiO<sub>2</sub>/ electrolyte interface [23,24,27] and values obtained in this study are given in Table 2. As seen from Table 2 the shortest electron lifetime ( $\tau_r$ ) is shown for the cell with liquid electrolyte and the highest for the cell with conventional gel polymer electrolyte. The results imply that the excited electrons in the liquid electrolyte based cell recombine with the I<sub>3</sub> in the electrolyte faster than in the gel electrolyte based cell [23,24,27].

The life time of the photoelectrons in the photo-electrodes increases in the sequence liquid < nano-fiber < conventional gel electrolyte. Therefore, the electron recombination rate at the photo-electrode/electrolyte interface changes in the order liquid > nano-fiber > conventional gel. If we consider the cell in open circuit, but under illumination, there will be an increase of the conduction band electrons in the same sequence with the highest values for the conventional gel. Therefore, the difference in the Fermi level and the redox level is lowest for the cells with the liquid electrolyte and highest for the cells with conventional gel electrolytes. This clearly explains the highest cell potential at low current densities obtained for the gel electrolyte based cell and the lowest cell potential at low current densities for the liquid electrolyte based cell as shown in Fig. 2.

#### 3.3. FTIR analysis

FTIR spectra of PVdF-HFP pure pellets and PVdF-HFP nanofibers in the region 450 - 1500 cm<sup>-1</sup> are compared in Fig. 4. Pure PVdF-HFP co-polymer is considered to be a semi-crystalline polymer showing FTIR peaks belonging to both the crystalline ( $\alpha$  phase) and amorphous ( $\beta$  phase) phases. Following the assignments of FTIR peaks to possible vibrations reported by Shau et al., Kumar et al.,



Fig. 4. Comparison of FTIR spectra of PVdF-HFP powder and PVdF-HFP nano fibers in the region 450 - 1500 cm<sup>-1</sup>.

and Abbrent et al., [17,28,29,30,31] for the pure PVdF-HFP pellets the FTIR peaks observed at 489 and 532 cm<sup>-1</sup> in the present work can be assigned to bending and wagging vibrations of the CF<sub>2</sub> group. The peak at 614 cm<sup>-1</sup> can be assigned to mixed mode of CF<sub>2</sub> bending and CCC skeletal vibrations. Peaks at 762 and 796 cm<sup>-1</sup> can be assigned to CH<sub>2</sub> rocking vibration and CF<sub>3</sub> stretching vibration respectively [28,29]. The peak at 839 cm<sup>-1</sup> can be assigned to mixed mode of CH<sub>2</sub> rocking while the peak at 879 cm<sup>-1</sup> can be associated with combined CF<sub>2</sub> and CC symmetric stretching vibrations [28,29]. The peak at 976 cm<sup>-1</sup> can be assigned to C–F stretching. These are the most significant peaks representing the crystalline phase of the polymer. Some peaks related to the amorphous phase are also observable and scaled up in Fig. 5.

It is interesting to see the slight shifts in the peak positions in the spectra of the PVdF-HFP nanofibers relative to the peaks of the pure PVdF-HFP pellets in the measured wavelength range. For example, the pure PVDF-HFP pellet shows a peak at 876 cm<sup>-1</sup> and apparently it has shifted to  $879 \, \text{cm}^{-1}$  for the nanofibers. From a comparison of FTIR spectra of different components in the DSSC electrolytes, some important conclusions with regard to the saltpolymer interactions can be drawn. The FTIR spectra of (a) PVdF-HFP nanofiber (b) conventional gel electrolyte (c) conventional liquid electrolyte and (d) PVdF-HFP nanofiber based gel electrolyte are compared in Fig. 5. The vibrational bands corresponding to the



Fig. 5. FTIR spectra of (a) PVdF-HFP nanofiber (b) Conventional gel electrolyte (c) liquid electrolyte and (d) PVdF-HFP Nano fiber based gel electrolyte in the region  $600 - 1500 \text{ cm}^{-1}$ .

amorphous phase ( $\beta$  phase) of the polymer can be observed at 840 and 879 cm<sup>-1</sup>, see Fig. 5 [32,33]. However, the dominant nature of peaks of the liquid electrolyte components and the presence smaller amount of the polymer have hindered the peaks of PVdF-HFP in the resultant spectra of PVdF-HFP nanofiber gel electrolyte, however it is worth to analyze this small peak further in order to understand the respective interactions. Conventional gel electrolyte shows spectra much similar to the spectra of the liquid electrolyte system as seen in Fig. 5.

In order to better understand the possible polymer-salt interactions in the electrolytes the peaks related to the  $\beta$  phase of the PVdF-HFP are elaborated further as it is difficult to use other peaks due to common peaks originating from the solvent phase in the electrolytes [29]. Two peaks related to the  $\beta$  phase are seen at 840.2 and 879.0 cm<sup>-1</sup> for the pure PVdF-HFP and they are slightly broadened for nanofibers. Due to the asymmetric nature of the peak shown around  $879.0 \text{ cm}^{-1}$ , it is deconvoluted in order to differentiate the two component peaks seen at 874 and 879 cm<sup>-1</sup>. The deconvoluted peaks are shown in Fig. 7(a) and (b). For pure PVdF-HFP, the two peaks are observed at 874.0 and 880.0 cm<sup>-1</sup>. However, for nanofibers these two peaks are visible at 874.3 and  $881.0 \text{ cm}^{-1}$ . These peaks around  $874.0 \text{ and } 880.0 \text{ cm}^{-1}$  can be attributed to C–F stretching and combined CF<sub>2</sub> and CC stretching vibrations [28,29,34]. Devin Hou et al. have identified the peak at about 880 cm<sup>-1</sup> as C–C skeleton vibrations [35]. The intensities of these two peaks have diminished for both nano-fiber based and convectional gel based electrolytes possibly due to the dilution effect of the liquid component.

As seen from Fig. 6, EC also shows a peak around  $893.0 \text{ cm}^{-1}$  and this peak is not visible in the PC spectra but can be seen in the EC and PC mixture at 893.3 cm<sup>-1</sup>. This peak has been assigned to ring breathing of EC [32,33]. However, the ring breathing peak of EC has split into two peaks for the salt added systems. This is possible due to the interaction between the K<sup>+</sup> ion and EC as previously seen for the Li<sup>+</sup>:EC systems [32,33,36,37]. This splitting has also been observed for alkaline cations in Raman spectra of EC in the similar frequency range [38]. The origin of this kind of split bands is believed to be resulting from the shift of the energy corresponding to the ring deformation (breathing) from the unperturbed configuration to the one interacted with cations [38]. The splitting is not so prominent and visible in Fig. 5 because the figure is scaled to describe the peaks with higher intensity. The shift of the split band is proportional to the magnitude of the induced polarization, and the polarizing power of K<sup>+</sup> is generally proportional to the charge density of the cation so it is less than that of Li<sup>+</sup> [38]. Therefore, the peaks were deconvoluted using Gaussian fit to identify the two



**Fig. 6.** FTIR spectra of (a) PVdF-HFP pellets, (b) PVdf-HFP Nano fiber, (c) liquid electrolyte, (d) conventional + gel electrolyte, (e) EC and PC mixture, (f) PC, (g) EC and (h) PVdF-HFP Nano fiber electrolyte in the region of 800–920 cm<sup>-1</sup>. Inset: FTIR spectra of solvents and electrolytes.



Fig. 7. FTIR spectra of (a) PVdF-HFP, (b) PVdf-HFP Nano fiber in the region of  $858-902 \text{ cm}^{-1}$  and Gaussian fitted curves.

components related to EC and EC-K<sup>+</sup> interactions as shown in Fig. 8 for (a) liquid electrolyte, (b) nanofiber electrolyte and (c) conventional gel polymer electrolyte. The first peak in Fig. 8 can be attributed to the ring breathing mode of EC and the 2nd peak can be related to that of the K<sup>+</sup>-EC complex. Peak positions and peak areas correspond to the two peaks are given in Table 3. As seen from this Table, the area corresponding to peak 1 is the smallest for the nano fiber electrolyte. Consequently, the relative area of peak 2 is much larger than that of the other two electrolytes. Hence, it can be inferred that K<sup>+</sup> ions are more associated with EC in the nano fiber electrolyte. Therefore, the salt is more dissociated leaving lager fraction of free iodide ions available for the charge transport resulting in higher photocurrents for the nanofiber electrolyte based cells compared to the conventional gel electrolyte based cells. The highest photocurrent observed for the liquid electrolyte based cells can be a result of the faster charge transport caused by low local viscosity due to the absence of the polymer matrix.

The vibrational bands corresponding to the amorphous phase ( $\beta$  phase) of the polymer are observed at 840 and 879 cm<sup>-1</sup> but are not



**Fig. 8.** FTIR spectra and their Gaussian fit of (a) liquid electrolyte (b) nanofiber electrolyte and (*c*) conventional gel polymer electrolyte in the range  $886-902 \text{ cm}^{-1}$ .

so prominently visible for these electrolytes. These peaks may be related to inter-chain interactions within the polymer. In electrolytes, polymer chains are separated or/and polymer-polymer interactions are replaced by polymer solvent interactions. Therefore, the FTIR peaks related to the amorphous phase are not very significant in these electrolytes.

# 3.4. Thermal properties

DSC curves of EC, PC, PVdF-HFP pellets, PVdF-HFP nano fibers and PVdF-HFP gels are shown in Fig. 9 in the temperature range from -60 to 170 °C. The PVdF-HFP nanofiber and the pure PVdF-HFP show broader melting peaks compared to that of the PVdF-HFP gel electrolyte. The glass transition temperature of pure PVdF-HFP is previously reported at  $-35 \degree C$  [28] but we observed its onset at -34.5 °C (inset of Fig. 9). The broad endothermic peak observed at 130-150 °C which is related to the melting of the polymeric components of the electrolytes is also observed for pure PVdF-HFP as was already reported by other workers [28,39]. In the present study pure PVdF-HFP has shown the melting peak at 145.5 °C whereas PVdF nano fibers has the melting transition at 141.7 °C. The melting temperature of the polymer nanofiber is thus lower evidently due to the nanosize effect. However, the melting peak of the PVdF-HFP gel electrolyte (curve (a)) is relatively narrow and appears at 145.8 °C. None of the electrolytes shows any

#### Table 3

Peaks of fitted curves of FTIR spectra for pure PVdF-HFP and PVdf-HFP Nano fiber in the region of 858-902 cm<sup>-1</sup>.

Electrolyte Type	Peak 1/cm <sup>-1</sup>	Peak 2/cm <sup>-1</sup>	Peak 1 area/a.u.	Peak 2 area/a.u.
Liquid	892.3	896.3	0.11	0.22
Nano	892.0	895.5	0.05	0.21
Gel	892.3	896.0	0.09	0.20



Fig. 9. DSC thermograms of EC, PC, PVdF-HFP pellets, PVdF-HFP nanofiber and PVdF-HFP conventional gel electrolyte in the temperature range of 100-170 °C.

# Table 4 The melting enthalpies of the pure PVdF-HFP and the PVdF-HFP nanofiber.

Electrolyte type	Peak Area/mJ	Weight/mg	$\Delta H_m/J \; g^{-1}$	Relative crystallinity/%
Pure PVdF-HFP	48.17	18.08	2.66	2.54
PVdF-HFP Nano fiber	24.00	10.52	2.28	2.17

significant thermal transition in the temperature range from 0 to 100 °C. Therefore, the electrolyte appears to be thermally stable in the temperature range where solar cells generally operate.

The melting enthalpies of the pure PVdF-HFP and the PVdF-HFP nanofiber samples shown in Table 4 were calculated using the peak areas in order to estimate the relative crystallinity [34]. The melting enthalpies of pure PVdF-HFP and PVdF-HFP nanofibers are 2.66 and 2.28 Jg<sup>-1</sup> respectively. Therefore, the PVdF-HFP nanofibers have shown a 14.3% crystallinity drop compared to that of pure PVdF-HFP. The melting enthalpy of 100% crystalline PVDF-HFP can be assumed to be 104.7 Jg<sup>-1</sup> [11]. The relative crystallinities of pure PVdF-HFP and PVdF-HFP nanofiber samples calculated in this study are tabulated in Table 4.

#### 4. Conclusions

In this study, we successfully fabricated PVdF-HFP polymer nanofiber membranes using electro-spinning technique. SEM images revealed the formation of membranes consisting of a threedimensional network of polymer nanofibres with average membrane thickness of  $14 \,\mu\text{m}$  containing nanofibers of diameters between 100 and 300 nm. Three types of electrolytes were prepared, (a) liquid electrolyte with KI dissolved in PC, (b) polymer nanofibre gel electrolyte by soaking the nanofibre membrane in the liquid electrolyte and (c) conventional polymer gel electrolyte by mixing the polymer directly with the liquid electrolyte. Dye sensitized solar cells were fabricated using these three electrolytes. The electrolytes were characterized by FTIR and DSC measurements and the DSSCs fabricated with these electrolytes were characterized by *J-V* and EIS measurements and their performance were compared.

Interactions between the cation (K<sup>+</sup>) and EC in the electrolytes were compared for the three electrolytes using the FTIR spectra showing a result compatible with a small prevalence of solvation for the nanofiber electrolyte. The shift in the polymer combination band at  $876 \text{ cm}^{-1}$  is also compatible with a reduced inter-chain interaction in the polymer for the nanofiber electrolyte. DSC thermograms showed that the glass transition temperature of the pure PVdF-HFP polymer was seen at -34.5 °C. A broad endothermic peak at 130–150 °C which is related to the melting of the electrolytes is also observed for the pure PVdF-HFP as already reported by other groups. DSC thermograms revealed that the crystallinity of the PVdF-HFP nanofiber sample is 14.3% less compared to that of pure PVdF-HFP polymer. The pure PVdF-HFP has a melting peak at 145.5 °C whereas PVDF-HFP nanofibers show the melting transition at 141.7 °C. The reduction of the melting temperature of the nanofiber sample is evidently due to the nano-size effect. However, the relatively narrow melting peak of PVdF-HFP gel electrolyte at 146.6 °C is due to the formation of polymer solvent complexes. Both electrolytes do not show any significant thermal transition in the temperature range where solar cells operate.

The DSSCs fabricated with nanofiber gel electrolytes offer an energy conversion efficiency of 5.3% and give  $V_{OC}$  and  $J_{SC}$  values comparable with those of liquid electrolytes under standard AM 1.5 solar irradiation. The  $V_{OC}$ ,  $J_{SC}$  and efficiency values for the nanofiber gel based solar cells are higher than those for the conventional gel polymer electrolyte based cells. This suggests the possibility of using electro-spun nanofiber membranes to trap liquid electrolyte and to form the gel state thereby minimizing some major drawbacks associated with liquid electrolyte based solar cells while improving the long term stability. Further improvements of this type of quasi solid state cell assembly and fabrication would help to augment the photovoltaic performance even further.

#### Acknowledgements

The authors wish to acknowledge the research support provided by, Carl Tryggers Foundation for Scientific Research, the Swedish Research Council and Magnus Bergvalls Stiftelse.

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