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Efficiency Enhancement of Dye Sensitized Solar cells (DSSCs) by Atmospheric DBD Plasma Modification of Polyetherimide (PEI) Polymer Substrate

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Abstract

In this paper, the effect of the dielectric barrier discharge pre-treatment on the surface properties of the polyetherimide (PEI) substrate is studied. This is to enhance the power conversion efficiency of flexible dye sensitized solar cell (DSSC) fabricated on the PEI substrate. RF magnetron sputtering is used for the deposition of the ITO having thickness of 100 nm on the substrate. The TiO_2-P25 powder is used in the preparation of the photoanode paste without the use of any organic binder and doctor blade technique is used for the deposition of the TiO_2 paste. A reasonable increment in the efficiency of about 55% from the plasma treated substrate is achieved over the untreated substrate. This implies that DBD plasma modification of substrate has a strong positive effect on the efficiency of DSSCs.

1. Introduction

Dielectric barrier discharge (DBD) is an electrical discharge between two electrodes separated by insulating dielectric barrier [1]. Compared to other plasma processing techniques, the DBD has some advantages such as; it uses simpler and flexible electrode configurations, and can treat surfaces of various sizes and shapes [2]. In addition, the DBD technique has higher efficiency and speed processing, very low electric power input and operational cost. Usually DBDs are preferred over other atmospheric pressure plasmas (APPs) due to their intrinsic stability against arching [3]. In environmental applications, DBDs have been implemented, owing to the presence of reactive oxygen (ROS) and reactive nitrogen (RON) species. Moreover, the DBD methodology has the advantage of inducing surface modifications on a material exposed to it as the applied electric field energy is effectively converted to chemical and physical processes in gases [4]. For the polymer-based substrate treatment, atmospheric pressure DBDs are the most effective plasma sources and therefore, its effects on the surface properties of various polymer materials are extensively examined and reported in literature.

The awareness in green and clean energy across the globe is in increase, and solar cells fabricated is expected to be free from environmental pollution [5]. The third-generation solar cells, particularly dye sensitized solar cells (DSSCs) are known to be promising renewable energy sources due to their low-cost, easy fabrication process [6].

Recently, there has been an increased demand for light-weight, flexible electronic devices as they can be produced in large scales using printing techniques at room temperature with a much-reduced production cost [7]. The concept of flexible polymer based solar cells is given much attention amongst researchers. In particular, the dye sensitized solar cells (DSSCs) using flexible, thin, and light weight conducting plastic films as photo electrode substrate are attracting considerable attention [8]. However, two major limitations with the plastic based substrates are the lower efficiency compared to glass substrate DSSCs and their thermal instability at the high temperature (450-500^{0}C) during sintering of TiO_2 photo electrodes. [9] introduced the press method for low temperature (< 150^{0}C) preparation of nano-structured TiO_2 photo electrodes having efficiency of 5.5% under 10mW/cm^2 (0.1 Sun) irradiation. Subsequent modifications based on the low temperature press method yielded efficiencies less than 6% under full irradiation at 10 mW/cm^2 has been reported. Lin *et al.* [10] also reported a binder free TiO_2 photoelectrode, sintered at low temperature (250^{o}C) on flexible substrate that produced an efficiency of 3.72%. Usually, Indium tin oxide (ITO) coated polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) are used as flexible base substrate for solar cells. A plastic substrate having higher thermal stability than that of the PEN or PET substrate may result in more efficient solar cell. Moreover, a pre-plasma treatment of the flexible substrate is the essential first step for increasing efficiency of solar cell as it improves adhesion between particle to particle or particle to substrate during solar cell fabrication.

In this work, the effect of DBD plasma surface treatment of polyetherimide polymer (PEI) substrate, followed by low temperature sintering of TiO_2 photo electrodes for DSSCs is reported. PEI substrate has higher thermal stability than PET and PEN substrates [11]. The surface properties of PEI substrate, crucial for solar cell efficiency, before and after plasma treatment and fabricate DSSCs using treated and untreated PEI are analyzed and compared. We have adopted low temperature method for preparation of nano-structured TiO_2 photo electrodes, as high temperature sintering may not be suitable for PEI substrate. This research is aimed at enhancing efficiency of dye sensitized solar cells (DSSCs) by atmospheric DBD plasma modification of polyetherimide (PEI) polymer substrate.

2. Materials and Method

2.1 Dielectric Barrier Discharge set-up

2.1.1 Schematic diagram of the experimental set-up

The schematic diagram of the DBD system as used by other researchers [12] is shown in figure 1. A 50Hz ac high voltage source is used to produce the discharge.

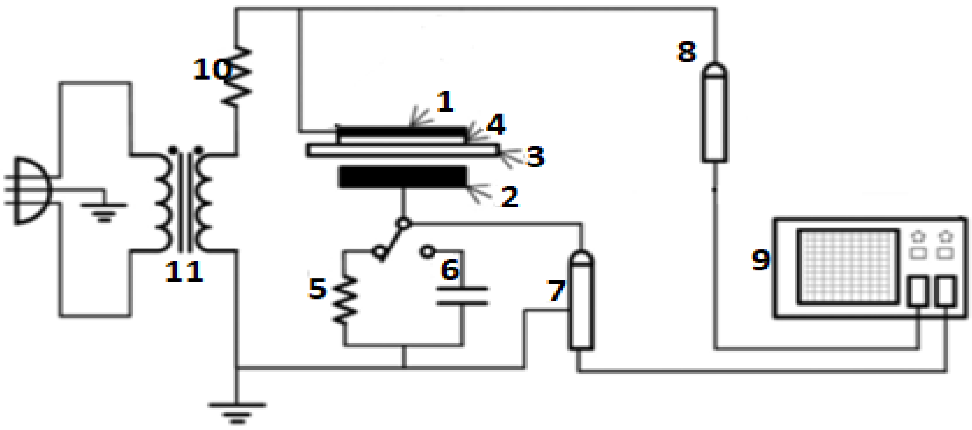

Figure 1 : Parallel plate DBD.

The gap distance between the stainless-steel electrodes with 50mm in diameter and 10mm in thickness, has been adjusted from 1mm~3mm. The DBD system was arranged in parallel-plate arrangement. The discharges were created in static atmospheric air in between the electrodes. The voltage applied to the electrodes were measured via a high-voltage-probe placing across the power supply. The discharge current and the transported charge were measured by a probe putting across a 302Ω resistor and 0.047μF capacitor respectively. The voltage and current waveform were recorded by Tektronix DPO3054 (500MHz bandwidth, 2.5GS/s sample rate) Digital Phosphor Oscilloscope.

The equivalent circuit of the discharge cell is shown in Figure 2. Here $C_{dielectric}$ and C_{air} represents the capacitance of the dielectric layer and the air gap respectively, while R_{plasma} represents the resistance of the plasma. Based on the equivalent circuit in Figure 2, the overall reactor capacitance of the discharge cell, C_{total} is determined through the summation of the reciprocal of the $C_{dielectric}$ and C_{air}

$$\frac{1}{C_{total}} = \frac{1}{C_{dielectric}} + \frac{1}{C_{air}} \quad (1)$$

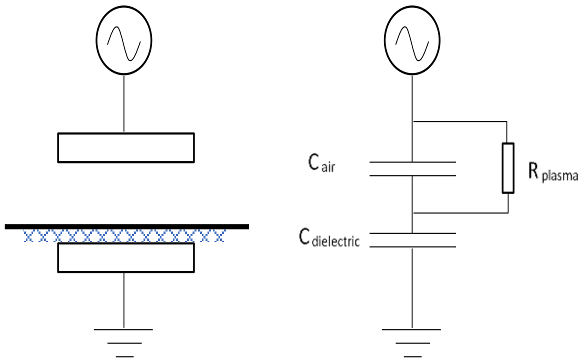

Figure 2. Equivalent circuit

2.1.2 PEI surface treatment

PEI substrate was purchased from Aldrich. Seventeen samples of 20 mm by 20 mm and thickness of 0.2 mm were cut out from the PEI. Glass plate with dimension of 10 cm × 10 cm and thickness of 2.0mm was used as dielectric material. The samples were cleaned with dish detergent to remove grease and contaminants from the surfaces of the PEI samples then dried at room temperature before placing on the lower electrode. Samples 1-6 were treated by varying the treatment time while the peak-peak voltage remain constant (20.5kV), samples 7-15 were treated by varying the peak-peak voltage while keeping the treatment time constant (60 seconds) and the remaining two other samples were left untreated as control for comparison.

The contact angles of all the samples were measured from profile of liquid droplets of de-ionized water on the material surfaces before and after treatment to evaluate the modification done on the surface of the substrate. The effects of the plasma treatment time and applied voltage on the contact angles were also studied. Ageing effect was determined by measuring the contact angles of the treated samples at different number of hours. The changes of the surface morphology of the untreated and treated samples were viewed by the Field Emission Scanning Electron Microscopy (FESEM) as it can provide topographical information of the samples. PEI-surface treatments were performed by setting the air gap to 3mm.

2.1.3 Electrical diagnostics of the discharge

The DBD discharge is in filamentary mode as evident from the multiple current spikes per half cycle of sinusoidal voltage in the oscilloscope. A charge-voltage Lissajous figure is a standard method for the electrical diagnostics of DBD discharges. Lissajous figures were plotted with instantaneous applied voltage along x-axis and instantaneous transported charge along y-axis. For smooth Lissajous figures, an average of 128 waveforms were taken. The dissipated electrical energy per one voltage cycle were determined by calculating the area under the Q-V plot of the Lissajous figure. The average powers consumed by the reactor also were calculated by taking the average energy multiplied by the applied frequency (50Hz). The reactor capacitance in different phase can be calculated from the slope of the vertical lines and horizontal lines of the Lissajous figure. The vertical lines represent $C_{dielectric}$ while the horizontal lines represent C_{total}.

2.2 Experimental methodology for DSSC fabrication

The DBD plasma treated and the virgin PEI substrates were employed for the nanocrystalline-TiO_2 film for the fabrication of flexible DSSC. ITO films were grown at 100 nm using RF magnetron sputtering technique on the surface of the treated and virgin PEI substrates in order to make the substrates conductive and still transparent. The sputtering system that was used utilizes a sintered ITO target having an In_2O_3:SnO_2 compositions of 90:10 wt. % with 99.99% purity, two (2) inches in diameter and 4mm thickness. The substrate temperature during deposition was maintained at room temperature. The sputtering deposition was carried out in a pure argon atmosphere at a pressure of 8.6×10^{-4} Torr and the sputtering power of 100W. Before applying the TiO_2 paste (photoanode paste) on the ITO/PEI, the sheet resistance (R_s) of the ITO was measured using multimeter to determine which side of the PEI is conductive. Then, the conductive surface of the ITO/PEI was placed faced up, and the edges of the PEI were covered using scotch tape leaving some active areas. The Scotch tape was used as a spacer to control the TiO_2 film thickness and to provide non-coated areas for electrical contact. After that, the photoanode paste was deposited on the conductive active area of the ITO/PEI using doctor blade technique and dried at room temperature. After drying, the TiO_2 thin films were sintered at 200^0C for 30 mins in air to give nanocrystalline-TiO_2 films. The thickness of the nanocrystalline-TiO_2 film was fixed at about 10µm for flexible DSSC. After the annealing process of the photoanodes, the substrates were soaked in N3 ruthenium dye solution for 24 hours. In order to control the environmental effect, the samples were stored in a closed and dark space. Meanwhile, the counter electrode was fabricated by depositing platinum on the conductive surface of the ITO/PEI. Lastly, iodine gel solution was applied in between the two electrodes as a mediator for the redox process. Then, the complete DSSC structure was obtained by sandwiching the working electrode and counter electrode together using a binder spacer.

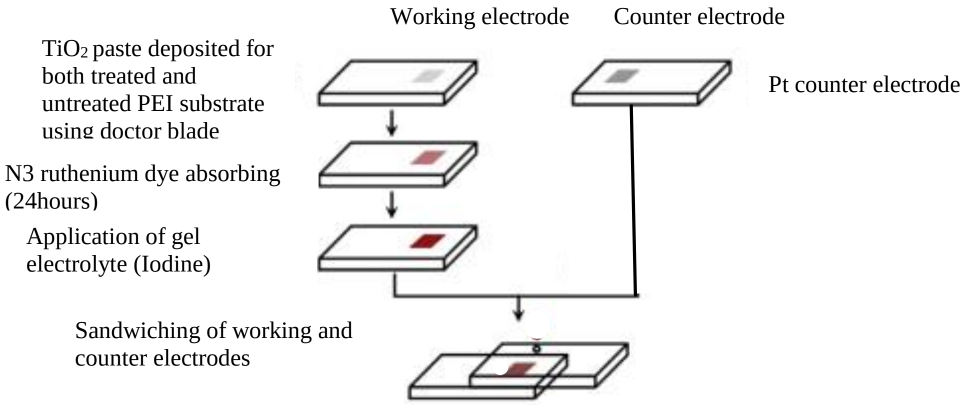

Figure 3: Process of fabrication of DSSC

3. Results and discussion

3.1 DBD plasma electrical characterization

The DBD discharge used for the treatment of PEI substrates operates in filamentary mode i.e. it is constituted by many tiny streamers distributed over entire area of the dielectric barrier [13]. The typical current voltage characteristics of the discharge is shown in Fig. 4.

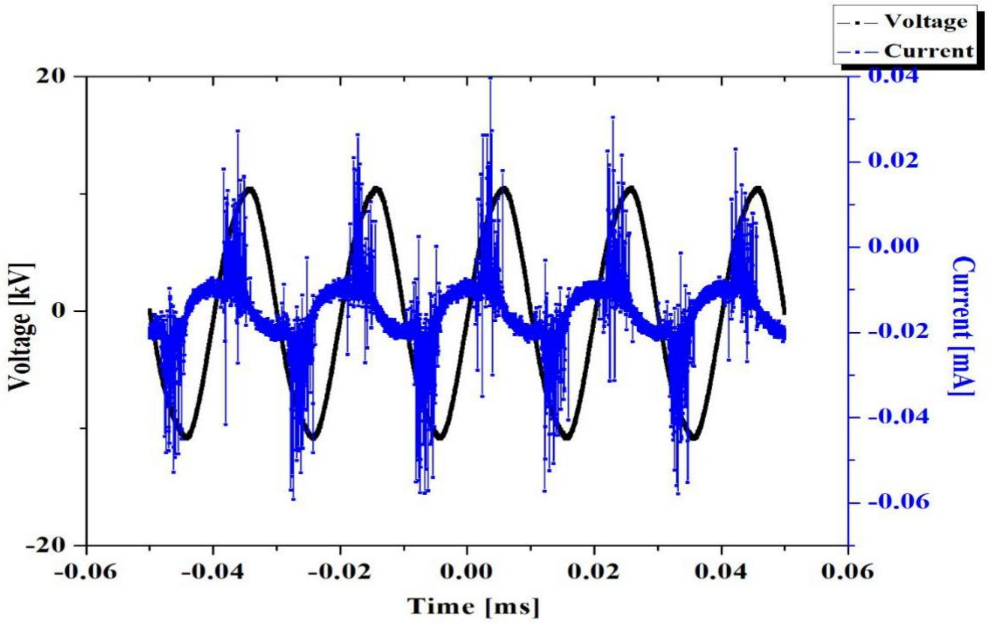

Figure 4: Current and voltage waveform of a DBD in air with inter-electrode gap of 3mm and 20.5kv peak-peak.

When the AC voltage applied to the DBD reactor reaches the onset value, the discharge starts in the air gap inside the reactor in the form of filamentary streamers [14]. The filaments are randomly distributed over entire electrode surface. Typical Lissajous figures of the discharge operated at various voltages (15.5 kV to 24.5 kV) is shown in Figure 5.

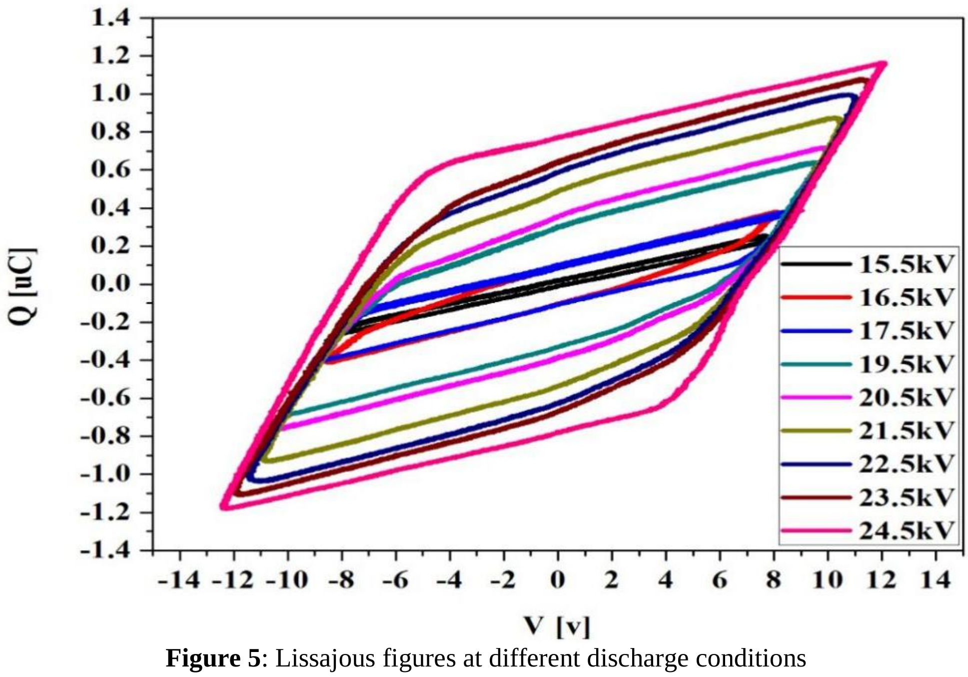

Figure 5: Lissajous figures at different discharge conditions

The corresponding values of the average power deposition and energy density is shown in Fig. 6. It is observed that there is a regular increase of the average power and energy deposition as a function of the applied peak to peak voltages. However, as it will be shown, there was no considerable change in the contact angle for samples treated with applied voltage higher than 20.5 kV. Therefore, the fabrication of the solar cell using dye synthesized method was carried out with the samples treated at 20.5 kV. The values of the parameters determined from the Lissajous figure is given in Table I for a 20.5 kV peak to peak voltage. The crucial parameter for surface treatment of polymer surface is the deposited energy density on the substrate and it is determined from the Lissajous figure by dividing the product of the discharge power and the treatment time by the effective discharge area. Figure 6 represent the variation of energy density as a function of treatment time at a fixed value of operating voltage. From figure 6 it could be observed that energy density increases with increasing treatment time. This is as a result of increasing the peak to peak voltage. It is evident from the figure that the deposited energy density increases linearly with treatment time.

Table I: Computed discharge parameters at 20.5kVpeak-peak applied voltage

Parameters	Values	Units
C_d (Dielectric capacitance)	0.0605	µf
C_T (Total capacitance)	0.03547	µf
C_g (Discharge gap capacitance)	0.0857	µf
V_b (Break down voltage)	16.2	V
E (Energy dissipated)	0.0083	J
A (Discharge area)	28.278	cm^2
P (Power dissipated)	0.415	W
f (Frequency)	50	Hz

3.2 Contact angle measurement

Dynamic contact angles of the samples were monitored by sessile droplet contact angle attention. A de-ionized water droplet of 1-2µl was gently brought into contact with the surface using a precision needle mounted on a movable stage, and the contact angles were measured immediately after the droplet stopped spontaneously advancing on the surface. The reported contact angles are the averages of four repeated measurements and the standard deviation was also calculated as the error bar.

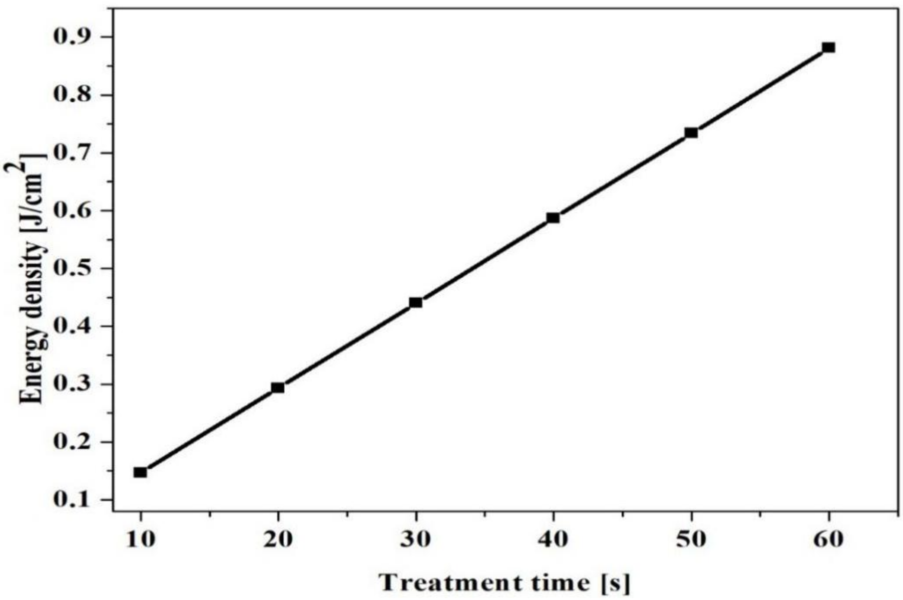

Figure 6: Variation of treatment time with the computed energy density for 20.5kV peak-peak

Figure 7 shows the values of the contact angles measured on a PEI polymer treated for a set of fixed discharge parameters (60seconds and 3mm gap) at various peak-peak voltages. The values of contact angle were lowered compared to untreated sample, due to DBD plasma surface treatment. These reductions of the contact angles in the treated samples, shows strong increased in hydrophilicity, induced by the air-DBD. When polymers are exposed to atmospheric plasma the energetic species (electrons and UV photon) in the plasma breaks the weaker C-C and C-H bonds on the polymer surface.

Atmospheric air plasmas are abundant of reactive oxygen atoms which react with the dangling bonds on the polymer surface forming different species such as mono-oxidized C-O, C-OH carbons, bi-oxidized C=O or O-C-O carbons and tri-oxidized O-C=O carbons. These oxygen-related polar groups are responsible for the enhanced hydrophilicity of the DBD treated polymer [4;13]. The contact angle, measured after 2 days of surface treatment, decreases abruptly with the increases of peak to peak voltage, reaching a minimum value of 36^0 at 22.5 kV and then, varies slowly with the applied voltage.

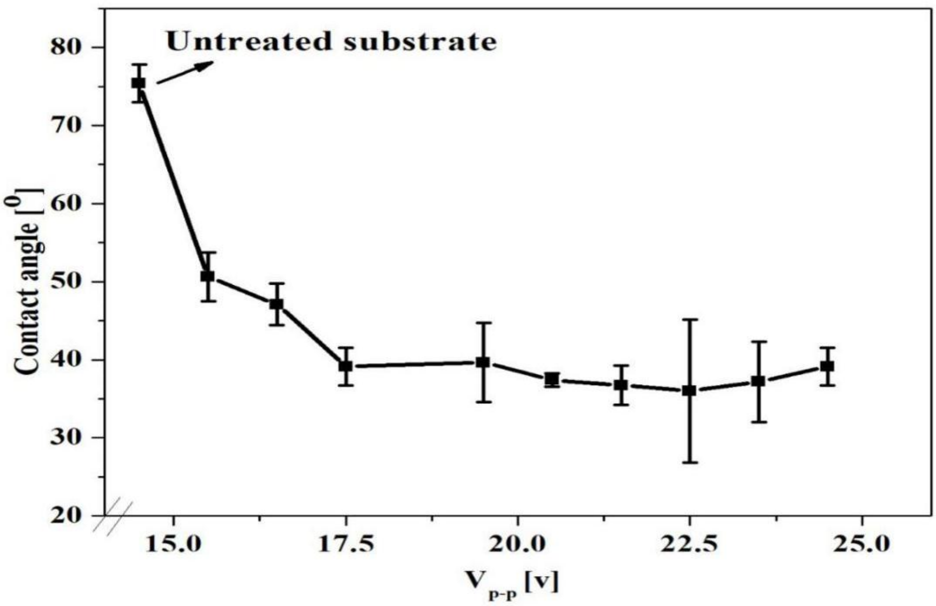

Figure 7: Ageing effect of the variation of contact angle with peak-peak voltage

Figure 8 shows the values of the contact angle measured on a PEI film treated for a set of fixed discharge parameters (20.5kV and 3mm gap) at various discharge time. After one day of treatment, the contact angle observed is found to change from 74.1° for the untreated sample to the minimum value of 21.3° associated with the 60secs of surface treatment, i.e. more than 60% reduction from the initial value. After two days of surface treatment, the minimum contact angle is 26.1° with 60secs of treatment which is higher than the initial value of 21.3° and later increases to 34.3° after three days of surface treatment, as shown in figure 9 above. This hydrophobic recovery is as a result of continuous chemical reactions from the remaining active radicals on the PEI surface with O_2 or moisture in ambient air or free rotation of the O_2 containing hydrophilic polar groups into the inside of the polymer [15]. Based on the contact angle measurement, the surface with the highest hydrophilicity (22.5 kV, 60 secs) has been chosen for the FESEM and fabrication of DSSC.

3.3 FESEM Analysis

Figure 8-9 shows the results of FESEM analysis of the treated and untreated samples respectively. Before the FESEM analysis the two samples were coated with platinum in order to make them conductive and suitable for FESEM analysis. It can be seen that the untreated PEI film is roughly smooth and clean without specific morphological aspects at the present scales of 1μm which is in agreement with that of [16]. As shown in Fig. 10(a)-(b) both FESEM images of the treated PEI films emphasize the obvious physical effects on the surface due to DBD plasma treatment. Formations of more clusters are seen on the surface of PEI film after DBD treatment which indicates the etching effect of it which can improve wettability [17].

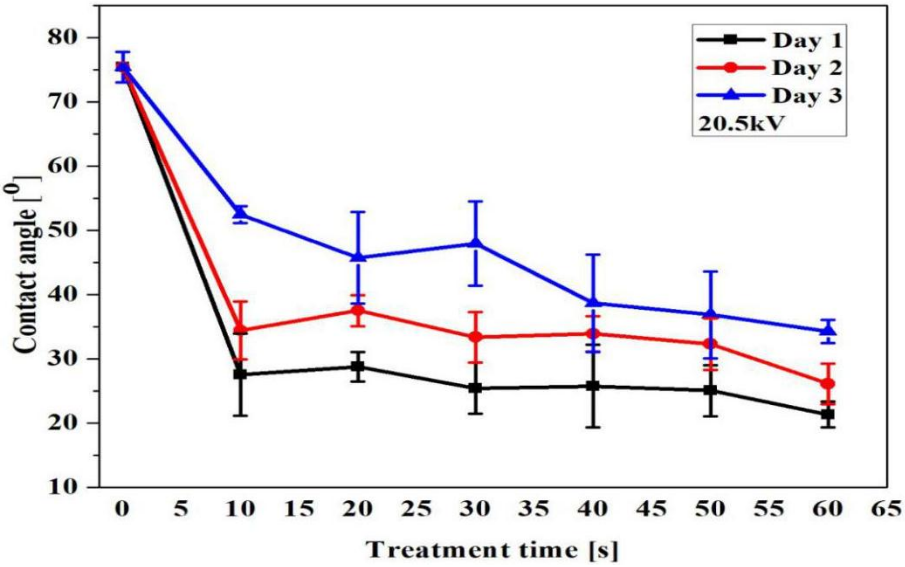

Figure 8: Ageing effect of the variation of contact angle with treatment time

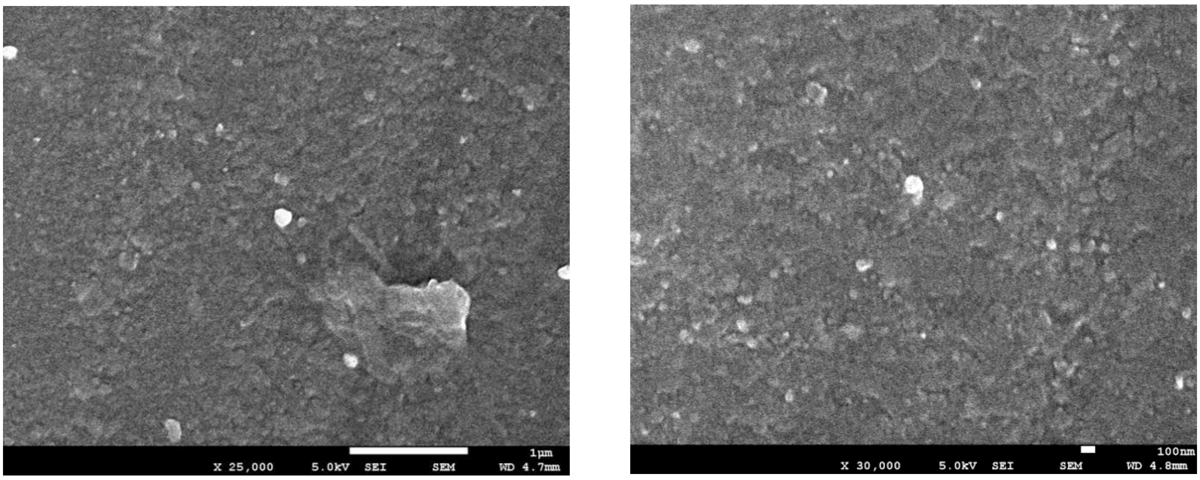

Figure 9: FESEM analysis of untreated PEI polymer with platinum coating

3.4 J-V Characteristics of DSSC

DSSCs were fabricated on the 100nm-ITO coated untreated and DBD plasma treated PEI substrate using the procedure mentioned in the section 2.2. Figure 11 (a)-(b) represents the J-V characteristics of DSSC fabricated on the treated and untreated PEI substrate, respectively. A short circuit current density (J_{SC}) of 11.4 mA/cm^2, open-circuit voltage (V_{OC}) of 0.63 V, and a fill factor (FF) of 0.39 were obtained for the ITO (100nm) /TiO_2- 3-layers (□10μm) plasma treated PEI based DSSC. For ITO (100nm)/TiO_2-3layers (□10μm) untreated PEI based DSSC shows a short circuit current density (J_{SC}) of 5.4mA/cm^2, open-circuit voltage (V_{OC}) of 0.54V and fill factor (FF) of 0.46. The former DSSC shows an efficiency of 2.8% compared to the later having an efficiency of only 1.34%. It shows that DBD plasma treatment on PEI polymer has a strong effect on the efficiency of a DSSCs. Dong et al.[1] have reported a solar cell efficiency of 3.05% prepared by doctor-blade method on ITO coated PEN (poly (ethylene naphthalene-2,6-dicarboxylate)) substrate. However, their process involves high temperature chemical sintering. Although, the optimal efficiency of the DSSC cell in our study is 2.80%, we believed that it is the novel attempt to prepare DSSC cell on flexible PEI substrate without involving chemical sintering.

Our results show that PEI substrate have the potential to be used as suitable conventional solar cell substrate alongside PEN or PET. However, most of the commercially available PEN or PET have ready made ITO coatings on it. But in this work, ITO using RF magnetron sputtering technique was deposited. This technique provides us another control knob for maximization of solar cell efficiency in future endeavors.

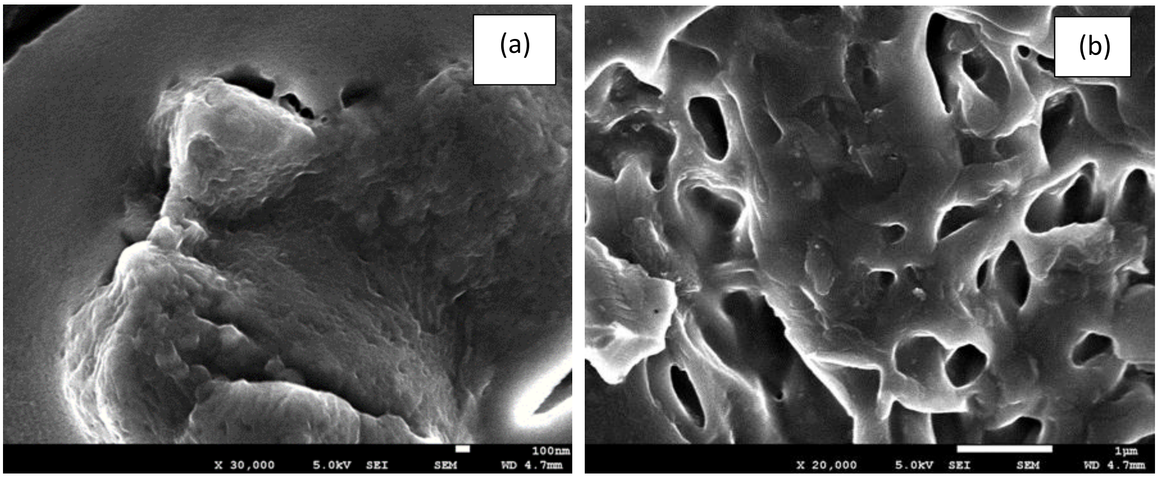

Figure 10: FESEM analysis of DBD treated PEI polymer with platinum coating at (a) 100nm and (b) 1µm magnification

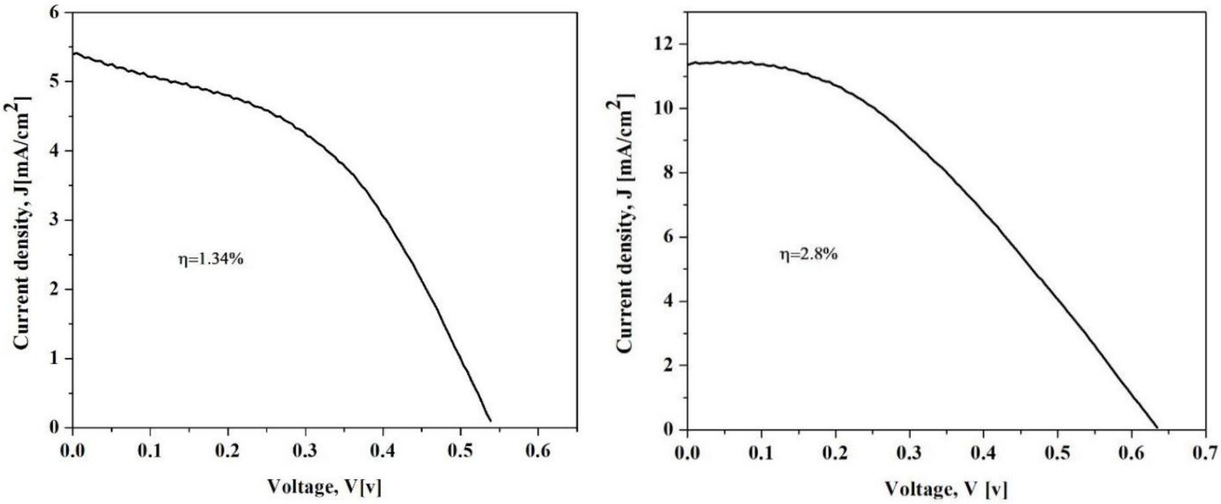

Fig.11 (a) J-V curve of the DSC fabricated on untreated PEI (b) J-V curve of the DSC fabricated on DBD plasma treated PEI

Conclusions

The effects on the flexible PEI substrates treated by dielectric barrier discharge (DBD) plasma technique has been investigated and contact angle technique has also been used for assessing the modification of the substrates. The ITO films were deposited at normal room temperature by RF magnetron sputtering from a ceramic target of ($ln2O_3$:SnO_2) 90:10wt% and 99.99% purity. The optimal surface treatment (20.5kV and 60secs) increased the conversion efficiency for PEI/ITO/Pt/gel-electrolyte/N3-dye/TiO_2/ITO/PEI DSSC to 2.8% being the best. This result shows that PEI polymer-based materials and manufacturing processes are suitable for flexible DSSCs. DSSC fabricated with untreated PEI substrate yield 1.34% efficiency. This implies that the DBD plasma modification of PEI polymer enhanced a conversion efficiency of DSSC by about 55%. It is concluded that DBD plasma surface modification of PEI polymer has a strong effect on the efficiency of flexible DSSC fabricated.

References

1. B. Dong, J. M. Bauchire, J. M. Pouvesle, P. Magnier, D. Hong, Experimental study of a DBD surface discharge for the active control of subsonic airflow. *Journal of Physics D: Applied Physics,* 41(15) (2008) 155201.

2. N. Dumitrascu, I. Topala, G. Popa, Dielectric barrier discharge technique in improving the wettability and adhesion properties of polymer surfaces. *IEEE transactions on plasma science,* 33(5) (2005) 1710-1714.
3. M. Laroussi & T Akan, Arc- free atmospheric pressure cold plasma jets: a review. *Plasma Processes and Polymers,* 4(9) (2007) 777-788.
4. G. Borcia, C. Anderson, N. Brown, Dielectric barrier discharge for surface treatment: application to selected polymers in film and fibre form. *Plasma Sources Science and Technology,* 12(3) (2003) 335.
5. A. Ossai, S. Ezike, & A. Dikko, Bio-synthesis of zinc oxide nanoparticles from bitter leaf (vernonia amygdalina) extract for dye-sensitized solar cell fabrication. *J. Mater. Environ. Sci, 11*(3) (2020) 421-428.
6. S. Saravanan, & R. Dubey, R. Study of Al-Doped and Al/N Co-Doped TiO2 Nanoparticles for Dye Sensitized Solar Cells. *J. Mater. Environ. Sci, 11*(1) (2020), 8-14
7. H. C. Weerasinghe, F. Huang, & Y. B. Cheng, Fabrication of flexible dye sensitized solar cells on plastic substrates. *Nano Energy, 2*(2), (2013) 174-189.
8. T. Yamaguchi, N. Tobe, D. Matsumoto, H. Arakawa, Highly efficient plastic substrate dye-sensitized solar cells using a compression method for preparation of TiO2 photoelectrodes. *Chemical Communications*, 45 (2007) 4767-4769.
9. A. Hagfeldt, M. Grätzel, Molecular photovoltaics. *Accounts of Chemical Research*, 33 (200) 269-277
10. L. Y. Lin, C. P. Lee, K. W. Tsai, M. H. Yeh, C. Y. Chen, R. Vittal, C. G. Wu & C. K. Ho, Low-temperature flexible Ti/TiO2 photoanode for dye- sensitized solar cells with binder- free TiO2 paste. *Progress in Photovoltaics: Research and Applications*, *20*(2), (2012) 181-190.
11. J. G. Liu, H. J. Ni, Z. H. Wang, S. Y. Yang & W.F. Zhou, Colorless and transparent high-temperature-resistant polymer optical films–current status and potential applications in optoelectronic fabrications. *Optoelectronics—Materials and Devices*, (2015) 57-81.
12. W. Tay, S. Yap, & C. Wong, Electrical characteristics and modeling of a filamentary dielectric barrier discharge in atmospheric air. *Sains Malaysiana, 43*(4), (2014) 583-594.
13. K. G. Kostov, T. M. C. Nishime, A. H. R Castro, A. Toth, L.R.D.O Hein, Surface modification of polymeric materials by cold atmospheric plasma jet. *Applied Surface Science,* 314 (2014) 367-375
14. K. Kostov, R. Y. Honda, L. Alves & M. Kayama, Characteristics of dielectric barrier discharge reactor for material treatment. *Brazilian Journal of Physics*, 39(2) (2009) 322-325.
15. Y. T. Cheng, J. J. Ho, C. K. Wang, W. Lee, C. C Lu, B. S. Yau, J. L. Nain, S. H. Chang, C. C. Chang, & K. L. Wang Improvement of organic solar cells by flexible substrate and ITO surface treatments. *Applied Surface Science,* 256(24) (2010) 7606-7611.
14. C. Zhang, T. Shao, K. Long, Y. Yu, J. Wang, D. Zhang, P. Yan, Y. Zhou, Surface treatment of polyethylene terephthalate films using DBD excited by repetitive unipolar nanosecond pulses in air at atmospheric pressure. *IEEE transactions on plasma science,* 38(6) (2010) 1517-1526.
16. T. Shao, C. Zhang, K. Long, D. Zhang, J. Wang, P. Yan, Y. Zhou, Surface modification of polyimide films using unipolar nanosecond-pulse DBD in atmospheric air. *Applied Surface Science,* 256(12) (2010) 3888-3894.
17. X. Li, H. Lin, J. Li, N. Wang, C. Lin, L. Zhang, Chemical sintering of graded TiO2 film at low-temperature for flexible dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry,* 195(2-3) (2008) 247-253.

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