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Research paper

Review on dye-sensitized solar cells based on polymer electrolytes

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Abstract

Dye-sensitized solar cells (DSSCs) have received significant attention due to easy fabrication process, environmental friendli-ness, low production cost, simple structure and high power conversion efficiency. This type of solar cell can convert visible light into electricity. Light is absorbed by a sensitizer, in order to harvest a large fraction of sunlight. Researchers reported DSSCs using polymer electrolyte exhibiting better stability than the DSSCs with liquid electrolyte. Overall solar (standard AM 1.5) to current conversion efficiencies over 9 % have been reached.

Keywords: *Dye-Sensitized Solar Cells; Polymer Electrolyte; Power Conversion Efficiency; Semiconductor*.

1. Introduction

Thin film solar cells are made from layers of semiconductor materials [1-5] and the film thickness may vary from few nanometers to several micrometers [6-10]. This second generation solar cells consist of cadmium telluride, copper indium gallium diselenide, dye-sensitized solar cell, and other organic solar cells. Mass production for thin film based solar cell is much cheaper as compared to traditional silicon based solar cell due to using less materials and lower cost manufacturing processes.

Nano-inspired energy conversion technologies, particularly excitonic solar cells, have recently been realized as potential alternates to replace the fast exhausting fossil fuels [11-13]. Dye sensitized solar cells (DSSCs), a hybrid excitonic photovoltaic technology, show exceptional characteristics features in terms of efficiency and cost of production [14-18]. DSSCs are considered to be cost effective due to the easy and straight forward fabrication procedures that can be executed through simple material processing and fabrication techniques. DSSCs employ wide bandgap nanocrystalline semiconductors as electron acceptors including TiO_2, SnO_2 and ZnO in various nanostructures, which simply transmit the visible spectral photons without a much of loss [19-21]. Various nanostructures are preferred in DSSCs to achieve effective electron transport, light scattering, and to tune the surface area which plays a critical role in photovoltaic performance of resulting DSSCs. An organic dye molecule layer, such as N719, Z907 and porphyrins, is coated onto the surface of the electron acceptor to generate excitons [22-25].

2. History of dye-sensitized solar cells (DSSC)

The solar radiation from the sun is approximately 3.8 million exajoules per year, which is 10,000 times the current energy demand [26]. The Bell laboratories designed first practical photovoltaic cell in 1954 using diffused silicon p-n junction technology with an efficiency of 6 % [27], [28]. Although the light to electricity conversion efficiency of silicon based solar cells has reached about 15 – 20 % [29]. However, the existing silicon-based solar cells are restricted to the terrestrial photovoltaic (PV) market due to their high manufacture and environmental costs. These limitations encouraged the search for low-cost, ecological solar cells. In 1972 the history of DSSC began with a chlorophyll sensitized zinc oxide electrode, first time, photons were converted into an electric current by charge injection of excited dye molecules into a broad band gap semiconductor. In 1991, O'regan and Grätzel built the first dye sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1 % under solar illumination, it was incremental, a synergy of structure, substrate roughness and morphology, dye photo-physics and electrolyte redox chemistry [30]. Titanium dioxide (TiO_2) became the semiconductor of choice. The material has many advantages for sensitized photo-electrochemistry such as biocompatibility, non-toxicity and inexpensiveness of material [31]. This simple structure material and low cost technology have further stimulated the great research interest to improve the efficiency of DSSC using tris(2,2-bipyridyl-4,4-carboxylate) ruthenium(II) dyes, liquid electrolytes, and platinum counter electrode which has attained ca. 10.4 % (100 mW/cm^2, AM 1.5), a level considered necessary for commercial use [32]. In 1993, industrial researchers have built solid foundations for product development. The Energy Research Center of the Netherlands (ECN) was one of the first European laboratories to bring DSSC technology development work to the sub-modules, and work began in 1995 [33-35]. They have developed the so-called masterplate for DSSC modules. The masterplate design of DSSC of ECN consisting of five individual cells, 2.5 cm^2 each, on a 7.5 x 10 cm^2 surface sandwiched between two fluorine doped tin oxide (FTO) coated glass substrates. The ECN researchers reported the results in 2003 of their semiautomatic system for the reproducible manufacture of DSSC in sizes up to 100 cm^2 [36, 37]. Manufacture of two types of glass DSSCs was examined: small-

area cells (less than 5 cm^2) with a conversion efficiency of 5.9 % for DSSC modules. During the two-year period 2002-2004, with association of four European universities (EPFL, Imperial College, Cracow University, materials Research center of Freiburg), three research institutes (ECN, Fraunhofer ISE of Germany, IVF) and one industrial partner (Greatcell Solar S.A.) cooperated under a European project called NANOMAX. The objective of NANOMAX was to test new strategies for the design of DSSC cells, cellular materials and manufacturing protocols with the aim of increasing efficiency to more than 12% under standard test conditions (AM 1.5, 1000 W/m^2) with good stability long-term [38, 39]. In addition, cost analyses were conducted to demonstrate the potential of DSSCs as a low-cost thin-film PV technology. Many companies such as Toyota, Sharp, Toshiba, Peccell technologies, Nippon, Dyesol and G24i has announced a DSSC module production of 25 megawatt capacity in 2007, with extension plans up to 200 MW by the end of 2008 [39-42]. Laboratories and companies such as ASIAN and Toyota Central labs to demonstrate various sizes and colors in a dye solar cell module connected in series at many international exhibitions and conferences reflect the potential role of dye-sensitized solar cell systems in technology photovoltaic [43-45]. In the near future, it is predicted that DSSC panels that have outstanding architectural appeal will be widely used in the commercial market. Within a few years, rigid and flexible products with lower costs will be available. Later in the decade, electro photochromic windows should be commercialized. During the next decade, it is possible to introduce water division devices in tandem [45].

3. Structure and working principle of dye-sensitized solar cells

The operational principle DSSCs is illustrated in Figure 1. The system is composed of few main components

(i) A transparent anode made up of a glass sheet treated with a transparent layer of conductive oxide (typically indium tin oxide coated glass and fluorine doped tin oxide);
(ii) A photo-anode composed of a mesoporous oxide layer (such as TiO_2) deposited on a transparent conductive glass substrate;
(iii) A monolayer charge transfer dye covalently bonded to the surface of the mesoporous TiO_2 layer to collect light and generate photon-excited electrons;
(iv) An electrolyte containing a redox mediator (such as I^- / I_3^-) in an organic solvent that effects the regeneration of the dye; and
(v) A counter electrode made of conductive glass substrate coated with platinum.

When the sunlight strikes the solar cell, the dye molecules collect photons and produce the excited electrons. The sensitizer injects excited electron into the conduction band of TiO_2 semiconductor film. The dye molecules lost electrons and then oxidized. The injected electron travels through the TiO_2 thin film toward the transparent conducting oxide (TCO) working electrode and are utilized to do useful work at the external load. The electrons now travel back through an external load and reach the counter electrode and thus complete the entire circuit. The performance of DSSC is generally evaluated by the different parameters of the cell such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), maximum voltage (V_m) and maximum current (I_m) of the cell. The overall performance of the DSSC can be evaluated based on power conversion efficiency (Z) and fill factor (FF) express as [46-48].

$$Z=\frac{Voc\ Isc\ FF}{Pin} \times 100\ \% \quad (1)$$

$$FF = Vm\ Im\ /\ Voc\ Isc \quad (2)$$

Where V_{oc} is the open-circuit voltage (V), J_{sc} the short-circuit current density ($mAcm^{-2}$), FF the fill factor, and Pin the power of the incident light. The photovoltage (V_{oc}) is determined by the potential difference between Fermi-level of electrons in the TiO_2 film and redox potential of electrolyte. Similarly, the photocurrent (J_{sc}) is determined based on the incident light harvest efficiency (LHE), charge injection and collection efficiencies. The efficiency (Z) of the solar cell can be defined as the ratio of electrical power to the optical power incident on the cell. The fill factor (FF) of the solar cell can be defined as the ratio of actual power (product of V_m and I_m) to the dummy power (product of V_{oc} and I_{sc}). The fill factor (FF) which is associated with the electron transfer process and internal resistance of dye-sensitized solar cells.

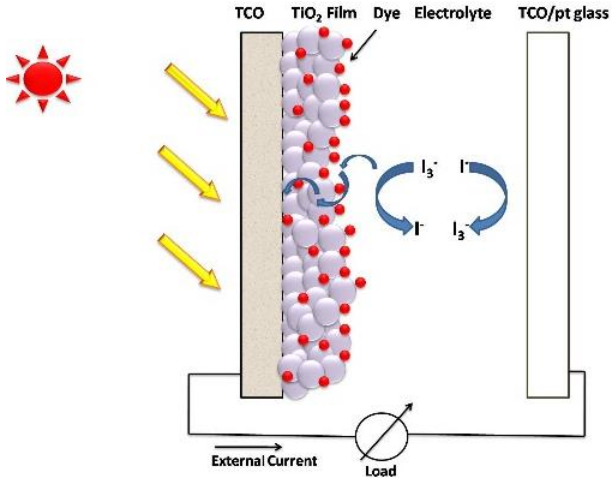

Fig. 1: Schematic Diagram of the Dye-Sensitized Solar Cells.

4. Characteristics of dye-sensitized solar cells

The efficiency of the device can be maximized by optimizing each of these three parameters (V_{oc}, I_{sc} and FF). For instance, high V_{oc} can be obtained by utilizing redox couple which has more positive redox potential and consequently increases the potential difference. Likewise, I_{sc} can be improved by utilizing panchromatic dye sensitizers that can absorb broad sunlight covering visible to the near-infrared range in solar spectrum. The fill factor is another paramount parameter that reflects the quality of solar cells. Increasing the shunt resistance and decreasing the series resistance as well as reducing the overvoltage for diffusion and electron transfer will lead to a higher FF value, resulting in higher efficiency and pushing the output power of the solar cell closer to its theoretical maximum. In fact, these parameters depend to a large extent on the properties of the material and the physical processes within the device. Consequently, the theoretical models that can capture the characteristics of physical process and the properties of the materials are fundamental to optimize various operating parameters and cell configurations.

Hole transport materials are considered as a major component in DSSCs as they determine efficient dye regeneration to avoid oxidation and hole transport. In general, liquid electrolytes are used as hole transporting materials in DSSCs along with a high work function metal as a hole collector. Redox couples such as iodide, cobalt, and polysulfide are few well known electrolytes that are being used in DSSCs [49]. While DSSCs show a remarkable photovoltaic performance, 13% efficiency, few major issues that are associated with functional materials impede the further development towards successful commercialization. Photon absorption of organic dyes in a spectral window (for example 350 nm – 750 nm), photo-electron injection into the conduction band of electron acceptor, charge transport in electron acceptor by diffusion, dye molecules regeneration, hole transport through electrolyte are the major physical process occur in DSSCs under illumination. It has been observed that interfaces between dye, electron acceptor, and electrolyte play a vital role on charge transport and recombination in the resulting DSSCs. The hole transporting electrolytes are considered to be one of the key components in DSSCs which are

responsible for effective hole transport, dye regeneration and eventually the open circuit voltage [50]. Stability, redox potential and ionic conductivity of the electrolytes are considered as important parameters to determine the performance of DSSCs. Conductivity of electrolytes is further depending the charge carrier mobility and concentration. Electrolytes in liquid state are highly preferred in DSSCs due to the compatibility with porous nature of electron acceptors through which the electrolyte can diffuse to form the junction on the dye coated surface. This arrangement facilitates the dye regeneration and hole transport throughout the bulk of electron acceptor and eventually the performance of DSSCs. However, few major issues that are associated with liquid electrolytes are identified as major performance limiting factors in DSSCs that include the volatility, conductivity, corrosive and flammable nature [51-52]. DSSCs employing liquid electrolytes for hole transport encounter serious issues in terms of stability over time due to the volatile nature of electrolytes even after proper sealing arrangement is made in the resulting DSSCs. Further, a high work function metal thin film, mostly platinum, is used in DSSCs as a hole collector from the electrolyte. The interface between platinum and liquid electrolyte becomes sensitive region due to the corrosive nature of electrolyte which affects the platinum electrode and its photo-catalytic activity during the solar cell operation. More than two decades of research and developmental works in the area of DSSCs address an urgent requirement of highly stable, environmental friendly hole transport materials to make the technology viable and affordable. Thus, development of alternate hole transporting materials for DSSC application has attracted much of scientific attention to address the major challenges that have been identified with liquid electrolytes. Further, the liquid electrolytes based DSSCs face major issues in terms of scale-up due to the difficulty of filling liquid electrolytes over large area. It is also observed that liquid electrolyte will impose major limitation in making flexible DSSCs. Confining such volatile and corrosive hole transport materials into flexible energy harvesting technology is rather challenging as the flexible material platform is highly preferred in the design and development of wearable opto-electronics in which only solid thin films have been demonstrated working well. Considering the stability and leakage related issues caused by liquid electrolytes in DSSCs, recently quasi solid state electrolytes were developed as hole transport material candidates which are basically in between solid and liquid states [53-55]. Studies have shown few major improvements in quasi solid state electrolytes based DSSCs in terms of stability and leakage [56], [57]. The major advantage of quasi solid state electrolyte is having diffusive characteristics of liquid while exhibiting cohesive property of solid. Quasi solid state hole transport materials are prepared by solidifying the liquid electrolytes by organic/inorganic gelators. The quasi solid state electrolytes are observed to be potential replacement for conventional liquid electrolytes to develop highly stable DSSC technology. Polymer electrolytes were introduced into DSSCs as alternate potential hole transport materials showing promising opportunity in terms of stability but critical issues in ionic conductivity [58], [59].

5. Literature survey

D.W. Kim et al reported DSSCs using polymer electrolyte exhibiting better stability than the DSSCs with liquid electrolyte [60]. It has been observed that liquid electrolyte in DSSCs causing stability related issues and this cannot be avoided due to the chemical nature. Room temperature ionic liquid based polymer electrolyte was developed and the resulting DSSCs showed an efficiency of 1.6% under 50 $mW.cm^{-2}$ illumination condition [61]. This study also reports the improved stability of the DSSCs due to the polymer electrolyte. Plasticizing effect and enhanced photovoltaic performance in DSSC was observed through doping of low viscous 1-ethyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), in polymer electrolyte [62]. In addition to improved ionic conductivity, the doping process was observed facilitating in reducing crystallinity of the polymer electrolyte in DSSCs which eventually helps to improve the performance. Ionic conductivity in polymer electrolyte is a major factor which determines the charge transport in DSSCs and it is observed that compositions, structure of the solvent and additives affect the ionic conductivity which eventually play a critical role in DSSC performance [63]. Further, increase in ionic conductivity in polymer electrolyte was achieved by adding poly(ethylene glycol)methyl ether to polymer electrolyte based on poly(epichlorohydrin-co-ethylene oxide), NaI and I_2 [64]. Table 1 shows the objective of research works and related experimental findings, which were successfully done by many researchers. In this work, polymer electrolytes were selected to solve some problems such as electrochemical stability, flammability issues, shape flexibility, leaking and sealing.

Table 1: Literature Review of Polymer Electrolyte Solar Cell

Authors	Objective of Research work	Result obtained
Ren et al. 2002	Ren et al., [65] investigated the PEO based gel network polymer electrolytes in dye-sensitized cells.	It was found that the PEO based gel network polymer electrolytes in dye-sensitized cells had comparable fill factor with the wet cell, giving energy conversion efficiency of 3.6 % and 2.9 % under 27 mW/cm^2 white light illumination.
Kim et al. 2004	Kim et al. [66] studied solid polymer electrolyte containing fumed silica nanoparticles.	It observes that composite polymer electrolytes consisting of PEODME, fumed nanosized silica, iodide salt and iodine provide improved DSSC performance at the solid state. The DSSC exhibited remarkably high conversion efficiency 4.5 % at 100 $mWcm^{-2}$, which is one of the highest values ever reported for DSSCs employing solid polymer electrolytes.
Kang et al. 2005	Kang et al. [67] demonstrated the studies of solid polymer electrolyte, especially PEO-KI/I_2	Kang et al. have achieved a remarkably high cell efficiency of 3.84 % at 100 $mW\ cm^{-2}$.
Joseph et al. 2006	Joseph et al. [68] introduce a new type of hybrid gel electrolyte matrix based on TEOS and PEG was developed for DSSCs.	It observed that the DSSC containing hybrid gel electrolyte rendered an open-circuit voltage of 0.74 V, a short-circuit photocurrent density of 9.2 $mAcm^{-2}$ and a fill factor of 0.61 at 100 $mWcm^{-2}$, and consequently an overall solar energy conversion efficiency of 4.1%.
Yang et al. 2008	Yang el al. [69] introduce a polymer gel electrolyte based on poly (methyl methacrylate) and its application in quasi-solid-state DSSC.	It was found that the quasi-solid-state DSSC possessed a good long-term stability and a light-to-electrical energy conversion efficiency of 4.78 % under irradiation of 100 $mWcm^{-2}$ simulated sunlight, which is almost equal to that of DSSC with a liquid electrolyte.
Singh et al. 2010	Singh et al. [70] have synthesized polyionic liquid electrolyte containing PVPI polymer which is suitable for DSSC.	It was observed that the iodide containing PVPI polymer rendered an open-circuit voltage of 0.70 V, and a fill factor of 0.30 at 100 $mWcm^{-2}$, and consequently an overall solar energy conversion efficiency of 0.65.
Sung et al. 2013	Sung at al. [71] analyzed the honeycomb-like organized TiO_2 photoanodes for solid-state DSSC.	It was observed that honeycomb like TiO2 demonstrated the open-circuit voltage of 0.74 V, and a fill factor of 0.58 at 100 $mWcm^{-2}$, and consequently an overall solar energy conversion efficiency of 7.4 %.
Bui et al. 2014	Bui et al. [72] prepared solid state DSSC based on polymeric ionic liquid with free imidazolium cation.	It was found that the dip-coated nanoporous TiO_2 electrode sensitized by N_3 ruthenium-based dye gave the conversion efficiency of up to 1.74 % and ionic conductivity up to 0.65 at 100 $mWcm^{-2}$.

Salvador et al. 2014	Salvador et al. [73] introduced a cellulose-based gel electrolyte for stable dye-sensitized solar cells.	It was found that the photoconversion efficiency bio polymer is up to 3.33%, open-circuit voltage of 0.67 V, and a fill factor of 0.24 at 100 $mWcm^{-2}$.
Rudhziah et al. 2015	Rudhziah et al. [74] synthesized biopolymer electrolytes based on blend of kappa-carrageenan and cellulose derivatives for potential application in dye sensitized solar cell.	It was observed that the light-to-electrical energy conversion efficiency of cellulose based biopolymer is up to 2.32 %. Open circuit voltage of 0.50 V and a fill factor of 0.64, under irradiation of 100 $mWcm^{-2}$ simulated sunlight.
Buraidah et al. 2017	Buraidah et al [75] have reported that polymer electrolytes have been produced by varying the amount of tetrapropylammonium iodide and 1-butyl-3-methylimidazolium iodide ionic liquid.	The optimized phthaloylchitosan based gel polymer electrolyte indicated power conversion efficiency and short circuit current density of 9.6 % and 19.7 $mAcm^{-2}$.

6. Conclusion

Dye sensitized solar cells indicate exceptional characteristics features in terms of efficiency and cost of production. Researchers have fabricated dye sensitized solar cells by using various polymer electrolytes, in order to compare and improved their efficiency. Currently, these types of solar cells can convert power up to 9.6 %.

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