A Review on Organic Photovoltaic Devices

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Abstract- Conventional energy resources like thermal power stations and nuclear reactors are threatening the environment by polluting it to the level that will be intolerable for us in near future. To overcome the difficulties, solar cell is the best alternative. It converts sunlight into electricity directly. This study reviews and describes some of the existing research on description of baseline organic solar cell (OSC) structures, advances in Organic Photovoltaic (OPV) research, types of OPV and search for new materials. Then, principle of operation, modeling approaches that have implemented either a one- or a two-dimensional drift-diffusion model to examine OSC structures are reviewed and finally limitations and challenge of the connection between simulation and experimental result have been discussed. There are many scopes to carry on research in this area because of the potential demand and many unresolved issues in this area of research field.

Keywords- Organic solar cell(OSC),Organic Photovoltaic(OPV), Drift Diffusion model, GPVDM

I. INTRODUCTION

Need of the day is environment-friendly renewable energy production because advancement of civilization demands more energy production. Conventional energy sources use fossil fuels and nuclear energy sources. Burning of fossil fuels produces green-house gases which in turn are responsible for global warming and related catastrophic events like extreme weather conditions, melting of ice in polar region etc. in addition the resources of fossil fuels are limited. Nuclear reactors on the other hand possess the threat of radioactive- wastages. To combat these potential threats from conventional energy resources solar cell is the best alternative. It converts sunlight into electricity directly. Having unlimited resource and providing green energy solar cells are real solution for the problems at hand. Today available inorganic solar cells mainly wafer based polycrystalline Si has highest efficiency of nearly 40%, though panel efficiency is limited to 15-20%. Si, CdTe, GaAs etc based thin film PV technologies are also emerging[1-3]. However, these devices have the disadvantage of high processing cost and for this reason inorganic solar cells have not been realised in large scale industrial and household uses. As a result, electricity generated from PV only accounts for less than 0.1% of the

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total worldwide energy generation [4]. Organic photo-voltaic (OPV) appeared in 80's as a possible replacement. The main advantages for using organic solar cells (OSC) are easy processing techniques, mechanical flexibility and huge stock of materials that can be tailored to desired level of band gaps (here difference between LUMO and HOMO level)[5-7]. Though initially power conversion efficiency (PCE) of organic solar cells (OSC) were very poor (1% in 1986 by Tang et al) few years of research has seen remarkable progress in this direction [8]. This paper aims to review mainly on OSC of different materials, its progress, different device structures and principle of operation in brief. Bulk Hetero Junction (BHJ) devices are most promising area of research among other various device structures. Our review article therefore aims to give special emphasis for BHJ devices, in order to improve device efficiency and to overcome possible degradation pathways. Numerical simulation of modelling device for optimization of different parameters in order to achieve higher efficiencies is recent trends of research. Therefore, a brief review on device modelling by simulation is also presented. Finally, justification for simulation results to reproduce experimental data is presented. The limitations and scope of further investigation are also presented in the same section.

II. ORGANIC PV SOLARCELLSYSTEMS

OPV solar cells composed of organic layers of semiconducting polymers (chains and bucky balls of p-type and n-type materials) [9] and oligomer materials [10] are characterized by the energy levels of HOMOs and LUMOs in these OPV materials similar to the respective valance bands and conduction bands of conventional inorganic semiconductors. P-type acts as donor (D) while n-type as acceptor (A) and combination of these two types of materials with suitable energy level alignments controls the device performance. In addition to that, hole transporting layers (HTL)such as poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) that blocks electrons while transporting holes to the anode of OSCs are usually coated on top of substrates that are smeared with indium tin oxide(ITO). This transportation increases the charge collection and enhances PV effect of the solar cell system [11]. Some widely used organic donor, acceptor and HTL materials are listed below:

Donor	Acceptor
poly(p-	poly(2,5,2',5'-tetraalkoxy-7,8'-
phenylenevinylen	dicyanodi-p-phenylenevinylene)
e) (PPV)	(CN-PPV)
poly(2-methoxy-	[6,6]-phenyl-C61-butyric acid
5-(2-	methyl ester (PCBM)
ethylhexyloxy)-1-	
4-	
phenylenevinylen	
e) (MEH-PPV)	
poly[2-methoxy-	poly(benzamidazobenzophenanthrol
5-(3',7'-	ine) (BBL)
dimethyloctyloxy	
)]-p-1-4-	
phenylenevinylen	
e (MDMO-PPV)	
poly (p-phenylene	poly [2-alkoxy-5-alkanesulfonyl-1-
benzobisthiazole)	4-phenylene vinylene](SF-PPV)
(PBZT)	
poly(3-	
hexylthiophene)	
(P3HT)	
HTL	
poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)	
(PEDOT: PSS)	

Table-I



Figure 1. Molecular structure of some polymeric donors, acceptors, and other material



Figure 2: HOMO and LUMO energy (eV) levels of commonly used OPV materials (Source: Gowsami et al., Adv.sol.Ener., Earthscan London)

III. ADVANCESIN OPV

First organic solar cell (OSC) was reported by C.W. Tang[12] in 1975, but its efficiency was quite low. A. J. Heeger, MacDiarmind and Shirakawa[13] discovered that the conductivity of conjugated polymers can be increased by doping. They win noble prize(2000) in chemistry for their contribution. By 1986, the OSC efficiency over 1% was achieved by C.W. Tang. Recently maximum organic cell efficiency of 18% is achieved [14-15]. At present, a huge development in the field of OPV technology is observed as a source of clean energy in terms of power conversion efficiencies(PCEs)[16].

Figure 2. shows continually increases in organic PV solar cell PCEs, with laboratory solar cell efficiency increased to ~18.2% in Fullerene based OSCs and ~17.7% in well-optimized OPV systems withn on-fullerene acceptor materials [17].



Figure 3: Increase in PCE efficiency of OSC (Source: IDTechEx Research)

IV. TYPES OF OPV AND SEARCH FOR NEW MATERIALS

The commonly investigated type of OSC structures include those based on the following:

- Bilayer organic semiconductor solar cell systems [18]. These cells consist of donor/acceptor bilayers and usually shows relatively low PCEs
- 2. Bulk heterojunction (BHJ) OSC systems, which essentially consists of a multilayer structure, are characterised by interactions between the donor and acceptor constituents. [19]
- 3. Dye-sensitized solar cells (DSSCs) [20]
- 4. Photo electrochemical cells (PCEs <0.1%) [21-22]
- 5. Perovskite solar cells [23]

Low PCE in bi-layer OSC has been attributed for the relatively small diffusion length of the excitons in organic materials. Most of the excitons created in the donor layer by absorbing the photon recombine before can dissociate into separate charge carriers. BHJ OSCs are produced as a blend of conjugated donor polymers such as P3HT and acceptor molecules like PCBM. By proper rationing of the donor and acceptor blends of BHJ OPV cells, the donor and acceptor molecules are situated at a distance which are within the order of exciton pair mean free path lengths (typically < 10 nm)[24] and enables most of the excitons to reach to the donor-acceptor interfaces where they can dissociate to form electron-hole pair. The structural factors of the blends of P3HT and PCBM have a significant role in improving performances of BHJ OSC systems.

Incorporation of a hole transporting layer between transparent conductor and P3HT and PCBM blend improves charge transportation and overall PCE. As a result, BHJ structured OPV devices, which are based mostly TCO/PEDOT:PSS/P3HT+PCBM/Al materials have been adopted and studied as baseline OSC structures[25]. These structures can be fabricated on top of flexible or rigid substrates. However, the material PSS(poly(styrenesulfonate) is acidic and strongly hydrophilic[26]. This hydrophilicity accelerates the solar cell degradation mechanism as a result of increased water moisture absorption. It does so by permeating the transparent conducting oxide(TCO) layer, which is called the ITO layer [27]. These permeation processes not only increase the degradation rates of the OPV systems but also introduce contamination in the structure. In order to remove the obstacles mentioned above while maintaining the practical requirements of the HTL materials, few researchers have demonstrated the idea of using transition metal oxides like molybdenum oxide (MoO₃) and vanadium $oxide(V_2O_5)$ instead of PEDOT:PSS [28].These Metal Oxides is found effective in prevention of unwanted chemical reactions and corrosion between the ITO-anode electrode and photoactive layers of OSCs.

Use of Graphene and its derivative as active material as well as buffer layer or as suitable electrodes has also been reported recently [29]. Graphene has remarkable electronic, optical and mechanical properties to be applied in the field of organic photovoltaic cells. Initially it was used as a replacement for transparent conducting oxide electrodes but graphene-based materials has been demonstrated to be useful not only as substitute for indium tin oxide electrodes, but also as cathode, electron acceptor, hole transport, and electron extraction material.[29-35]

V. PRINCIPLE OF OPERATION

Organic BHJ Solar cell generally uses a blended photoactive solid-state layer of organic donor and acceptor materials to be sandwiched between a transparent anode (commonly ITO) with large work function and a cathode (commonly aluminium) with small work function.(figure-4).Photo induced charge generation is comprised of the following steps [36]: Firstly, incident photons are absorbed by the donor polymer within solar cell structures and excitons are created inside the material. In order to have a prominent PV effect, the excitons must diffuse inside the OSCs to reach to the donor/acceptor interfaces. At the interfaces, the charges dissociate to form polarons, which are weakly bound pair of charge transfer complexes. In order to achieve optimized photo generation, transportation and charge collection at electrodes, the cathode Fermi energy should be less than the LUMO level of acceptor and the anode Fermi energy should be more than the donor HOMO level. This gives rise to the attractive combinations of electrical and optical properties that are significant for better OPV system performances. This has led to the development of an optimised empirical relation for predicting open-circuit voltage in OSCs with BHJ structures [37]



Fig. 4 Typical cell Structure of Organic OSC

Organic excitons, having charges bounded by strong electrostatic force with energy ~ 0.4 eV, in contrast to photo generated weakly bound excitons in inorganic semiconductors are not easily separated into free charge carriers. Their binding energy values are stronger than those of thermal energy at room temperature(0.02 eV). As a result of it, excitons could be dissociated into short lived and weakly bound polarons, at the donor/acceptor interfaces[38] only. This is why the photoactive layers of BHJ structured OSCs are made of permeating blends with phase separated donor and acceptor materials so that exciton mean-free path length is increased and so also their chance of dissociation [39]. The weakly bound polarons require further working to separate them into free charge carrier complexes. Their separation, transportation and extraction at electrode end are too dependent on local internal and external electric fields along with the ambient conditions (like temperature). This not only explains the role of work functions of the two electrodes but also puts emphasis on the significance of local morphological configuration of donor and acceptor materials, after phase separation through controlled thermal procedures[40]. Built in electric field from external electrodes due to difference of their work function helps the polarons to dissociate into free charge carriers, before being transported at the terminal electrodes for collection. However, the charge carriers can recombine during their journey to respective electrodes. It has been shown that, the charge carrier mobility, in absence of any hindrance such as impurities/defects, reorganization of chains etc depends largely on the morphology of blended photoactive layers [41].

In BHJ OSCs, the free charge carriers are transported primarily by hopping and drift diffusion translations through bi-continuous percolation paths within the photoactive layers. Along with this, these movements are also dependent on the characteristics of the internal and external electric field of the OSC systems. The electric field magnitude is determined largely by the work functions of the electrodes. At the electrodes, the holes at the anode and the electrons at the cathode can either recombine or get extracted by driftdiffusion process and give rise to the open-circuit voltage of the OSC system. Moreover, typical BHJ OPV systems having low bandgap blended donor/acceptor polymers[42] and those which are based on fullerene-free polymer structure[43] with comparatively high PCEs have been recognized and hence investigated widely.

In addition to the laboratory experiments, numerical modelling and computational analysis of PCE of OSC are performed. These analyses are based on cumulative augmentation of efficiencies collected from different mechanisms involved in OPV solar cell operation processes, starting from cell illumination to charge compilation and extraction at electrodes[44].

VI. MODELING OF BHJ OSC STRUCTURES

To make out the dependency of OSC performances on their material and structural properties, experimentally synthesized polymeric materials and their corresponding OPV devices are being investigated [42, 44,45], in addition to that, electrical models are also being developed[44,45]. These developed models are generally based on one spatial dimensional solar cell systems and concepts[44,47].But, recently, a two-dimensional space geometry modelling to study BHJ OSC structures are also applied by a number of research groups[48]. These models are used to investigate sensitive performance issues and associated limiting issues of OPV system performances [49]. To investigate the electronics and kinetic processes of different OSC system configurations, drift-diffusion based finite difference computational methods have been developed and implemented widely. These driftdiffusion electrical models are befitting to inorganic solar cell systems as well as to organic and inorganic LEDs and other semiconductor devices and components. This is due to the fact that the driving force responsible for migration of charge carrier in electronic semiconductor structures have been found to be quite similar for inorganic and organic semiconducting materials [50,51].

The finite difference continuum method is a combination of Poisson's and current continuity drift diffusion models [44]. The model is usually solved by iteration with appropriate self-consistent boundary conditions. For convenience, the models and the associated current continuity equations for electron and hole densities (which are function of position within the solar cell device) of a given PV system are often written and solved under steady-state condition. Both electrons and holes contribute to the photocurrent of semiconductor structures such as solar cells, as is well known. As a result, a set of postulates based on Poisson's equation and current densities for electrons and holes have been developed for evaluating the performance of PV devices. These postulates are written in a form that links electron and hole current densities to the electrostatic potential, which is also tied to the solar cell system's electric field intensity. Therefore, to predict the solar cell behaviours, the current density equations combine both drift and diffusion characteristic transport of charge carriers to formulate current density continuum models.

To obtain the solution of drift-diffusion models, the whole device is divided into a finite number of discrete grid units, using either the forward or the backward difference approximation method [52]. Moreover, in some recent numerical studies guidelines for modelling of appropriate boundary conditions for the charge carrier densities were also discussed. The absorption of photons inside photoactive semiconducting polymeric materials causes the production of OSC excitons, which then diffuse to the interfaces for dissociation. The literature[41] comprises a recent description of the exciton diffusion phenomenology for inclusion in BHJ OSC models. However, the photo induced excitons are only capable of diffusing across a certain distance known as exciton diffusion length mean free path. This implies that for modelling and simulation of OSCs, the effects of exciton diffusion on OPV operation must be taken into account. However, it is also found from studies that in BHJ OSCs, the distances between excitons and donor/acceptor interfaces are usually in the order of exciton diffusion length. As a direct consequence, the typical exciton diffusion efficiency in BHJ OPV devices is very close to 100 percent. This consideration allowed the excitonic diffusion processes to be neglected in the simulation of BHJ OSCs using electrical drift-diffusion models[44,49]. Hence, to calculate the net photo generation of electron hole pair density in OSC systems, the dissociation and recombination of excitons at donor/acceptor interface, are usually combined. There have been few other theories proposed to explain the generation, recombination and separation of electron hole pairs in free charge carriers in organic-like amorphous semiconductors. Among these theories, Langevin recombination[52], Onsager's geminate generation-recombination model [53,54], and its successful improvement by Braun [55] are notable. In general, Onsager's geminate generation-recombination model is applicable to OSC systems with weak electrolytes have refined it to derive the field-dependent separation rate constant theory. In case of a disordered polymer, fullerene based solar cell systems, the distance between electron and hole is found not to be constant throughout the device. As a result, it has been determined that the probability of electron-hole pair separation, in general can be calculated as integral over the spherical averaged Gaussian distribution of electron-hole pair separation distances[44]. After charge carriers are separated, they may still suffer losses during transportation to their respective electrodes at the solar cell's terminal due to a variety of factors.

These elements could include the Shockley-Read-Hall model [56 -57], the surface-assisted [58] and the trapassisted recombination, as well as bimolecular [59] recombination free charge carrier phenomenology. However. It has been found that though trap assisted recombination is dominant in OSCs with polymer-polymer structure, they do not show significant effects on OPV devices with polymerfullerene structures. As a result, the trap-assisted recombination has been ignored in the operation and modelling of OSCs with polymer-fullerene structures. This means that, during migration of charge carriers, the loss of

dominantly by charge carriers occurs bimolecular recombination. The bimolecular recombination model was modified to account for the charge carrier density gradient in BHJ amorphous organic semiconductor devices by Koster et al. The authors also revealed that in OSCs, the predominant bimolecular recombination rate is determined by the charge carriers with minimum mobility i.e. holes. The bimolecular recombination rate model was further extended by Deibelet al.[60] to describe the observed experimental recombination rates which is found to be lower than the Langevin recombination rate. This extension led to the description of the constant bimolecular recombination rate for the OPV devices. As reported by Koster et al., the net expression for the generation/recombination of charge carriers is obtained by combining the generation and bimolecular rate models.

To find the solution of the drift-diffusion model, either Gummel or Newton iteration scheme [61] are applied to solve basic Poisson and continuity equations. However, due to its simplicity, Gummel iteration scheme is more preferred than Newton scheme for numerical predictions and computational simulations. It is also worth noting that the values of the original parameters used in the drift diffusion equations, such as electron/hole densities and potential differences, may be very large. As a necessary consequence, the equations can be normalised, and the model was run with reduced variables (in arbitrary units) by employing appropriate carrier density and differential equation operator scaling factors.

VII. SIMULATION RESULTS VS EXPERIMENTAL DATA, LIMITATION AND SCOPE

Various simulation softwares are now available. One such software is the A General-Purpose Solar Cell Simulation tool GPVDM. Simulation by GPVDM software of a typical BHJ OSC data resembles experimental data to large extent though many aspects in experimental results could not be obtained through simulation. This shows that numerical simulations of a similar OSC with perfect planar contacts are closely mimicking the electronics, kinetics, and charge carrier transfer interfaces in actual structures of BHJ OSC systems. However, there are still many gaps between the experimental data and simulation results that need to be addressed. One of the major issues is the stability and degradation in case of organic PV devices.

VIII. CONCLUSIONS

Organic photovoltaic devices are of great importance of research topic because of its potential uses in large scale. Improvements of efficiencies of OPV by various ways are under way, such as choosing suitable donor/acceptor materials, suitable morphological control, design of devices and modelling OPV devices by simulation software's. Synthesis and use of new materials as active or transporting layers is also very important. Graphene based materials are one such promising candidate to be used many ways. Fastest way of improving efficiency of OPV devices is to use of simulation software's to find optimum materials, thickness, morphology and design and then to perform experiment in the lab accordingly and then to find if there be any mismatch between theoretical simulation and experimental data. So we think that there are many scopes to carry on research in this ever increasingly demandable area of research field.

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