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REPORT ON ROUTE TO SCALE-UP OF POLYMER BASED PV

Suggestions for Research and Technology

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PREFACE

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ABSTRACT

Solar power is the most abundant renewable resource on earth. In spite of this abundance solar power, only 0.04 percent of the energy used by humans comes directly from the sun because harvesting solar energy using photovoltaic technologies cost more than burning fossil fuels. Organic materials show a possibility for harvesting the sun's power more efficiently and economically than other photovoltaic technologies. This report provided an overview of the current state-of-the-art for organic photovoltaic technologies and discussed scientific issues that need to be addressed to facilitate commercial viability. The authors concluded that large– scale production and distribution of low-cost organic photovoltaic modules could potentially play an important role in greenhouse gas reduction and meeting global energy demands.

Keywords: California Energy Commission, renewable energy, research development and demonstration, California Renewable Energy Center, Solar energy storage, life cycle

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EXECUTIVE SUMMARY

Introduction

Use of fossil fuels is raising the levels of greenhouse gas in the Earth's atmosphere, which in turn threatens to cause climate change and unknown economic hardship. Conservative calculations show humankind must drastically reduce the amount of primary energy used on a daily basis and simultaneously shift to energy sources that result in reduced carbon emission intensity to avoid the largest risks for climate change. Solar power is the most abundant renewable resource on earth. In spite of this abundance, only 0.04 percent of the energy used by humans comes directly from the sun because harvesting solar energy using a photovoltaic panel costs more than burning fossil fuels. Organic materials have recently been intensively studied for photovoltaic applications. Organic materials do not have the capacity to harvest the sun's power more efficiently, but power generation from organic photovoltaic materials could cost considerably less than other photovoltaic technologies. The cost-per- watt savings comes from the potential of using flexible substrates, printable organic inks for the active layers, lighter weight materials resulting in reduced transportation expenditures, and reduced materials costs. The ability to use solution processes for deposition is particularly exciting because products such as automobiles, freight containers, and building materials could be painted with photovoltaic coatings, resulting in low cost, abundant solar energy.

Project Purpose

The goal of this project was to provide an overview of the current state-of-the-art for organic photovoltaic technologies and to discuss the scientific issues that need to be addressed to facilitate market-ready production.

Project Results

Several companies have started to produce organic photovoltaic (OPV) materials and have reported record power conversion efficiencies (PCEs) that cannot be matched by academic studies. This report focused on the scale-up of OPV materials to a reel–to–reel solution–processed and mass–produced product. The authors concluded that large– scale production and distribution of low-cost organic photovoltaic modules could potentially play an important role in greenhouse gas reduction and meeting global energy demands. The authors believed that research must still be conducted on emerging technologies such as flexible transparent electrodes, solution–processable electrodes (metal or transparent), developing reel–to–reel and spray coating methods, studying polymer morphology that results from the new coating methods, developing effective transparent oxygen gas (O_2) and water (H_2O) barrier materials, and learning to make all of these technologies work together.

Project Benefits

This report demonstrated that large–scale production and distribution of low-cost OPV modules could potentially reduce greenhouse gas emissions and help meet global energy demands for renewable power.

CHAPTER 1: Introduction

Use of fossil fuels is raising the levels of greenhouse gas in the Earth's atmosphere, which in turn threatens to cause climate change and unknown economic hardship. Conservative calculations show that in order to avoid the largest risks for climate change; humankind must drastically reduce the amount of primary energy used on a daily basis and simultaneously shift to energy sources that result in reduced carbon emission intensity.[1] It is well established that solar energy is by far the most abundant source of renewable energy. However, solar energy is difficult to harvest because it is a diffuse energy source that requires collection over large land areas and because the sun only shines during the day. Photovoltaics are a mature technology. The first silicon photovoltaic device was fabricated by Bell Labs in 1954. Since that time, photovoltaics have been greatly optimized and a power conversion efficiency (PCE) approaching the Schockley-Queisser limit for a single p/n junction of over 25 percent has been reported.[2]

Photovoltaics only contribute 0.04 percent of the world's total energy usage. The reason is that, although solar power is the most abundant energy source, conversion of solar energy into electricity or solar fuels is far more expensive than burning fossil fuels.[3] Government incentives to install photovoltaic capacity has resulted in growth for the solar industry of over 30 percent per year for the last decade, but this growth curve is still too low to significantly reduce global greenhouse gas production, due to rising energy demand. The DOE report on Basic Energy Needs for Solar Energy Utilization recommends development of a new class of photovoltaic collectors that are able to produce more Watts per dollar.[4] Fig. 1 shows a chart with power conversion e_ciency vs cost in US$ per m2 for a PV unit. On the chart are marked three zones that represent technological and economic challenges for PV production. All of the PV devices that are currently commercially available fall into Zone I. Solution-processable organic photovoltaics (OPV) are currently being intensely investigated because this technology represents the best chance for developing a PV product in Zone II. The major advantages of using conjugated organic materials for PV units rather than inorganics are the low material and substrate costs and the ease of printing and fabrication. However, OPV devices are currently far less efficient and have shorter lifetimes than inorganic solar cells. The combination of low material and fabrication costs for OPV promises to reduce the unit cost by ~10x.[5] This cost savings is based on the idea that mass production will decrease material costs and that

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1 N. S. Lewis, Powering the planet, MRS Bull. 32 (2007) 808–820.

2 M. A. Green, K. Emery, Y. Hishikawa, W. Warta, Solar cell efficiency tables (version 34), Prog. Photovolt. 17 (5) (2009) 320–326.

3 N. S. Lewis, Powering the planet, MRS Bull. 32 (2007) 808–820.

4 Basic research needs for solar energy utilization, Tech. rep., Department of Energy (2005).

5 C.J. Brabec, J.A. Hauch, P. Schilinsky, C. Waldauf, Production aspects of organic photovoltaics and their impact on the commercialization of devices, MRS Bull. 30 (1) (2005) 50–52.

fabrication can be performed in a reel–to–reel format onto flexible substrates. The resulting economic balance will yield a reduction in the cost-per-Watt for power produced from OPV devices when the device power conversion e_ciency nears 10 percent. Zone III is shown more as an inspirational/political goal rather than an engineering challenge with a real chance of near term success. There are currently no viable technology paths that promise to both reduce module cost and also increase e_ciency beyond the Schockley–Queisser limit.

Far more basic and applied research is needed to develop OPV to become a viable large–scale electricity source. This report discusses the state-of-the-art for organic photovoltaics and addresses scientific and technological hurdles that must be overcome for scale–up to commercialization. A discussion of cost is found in Refs [6] [7].

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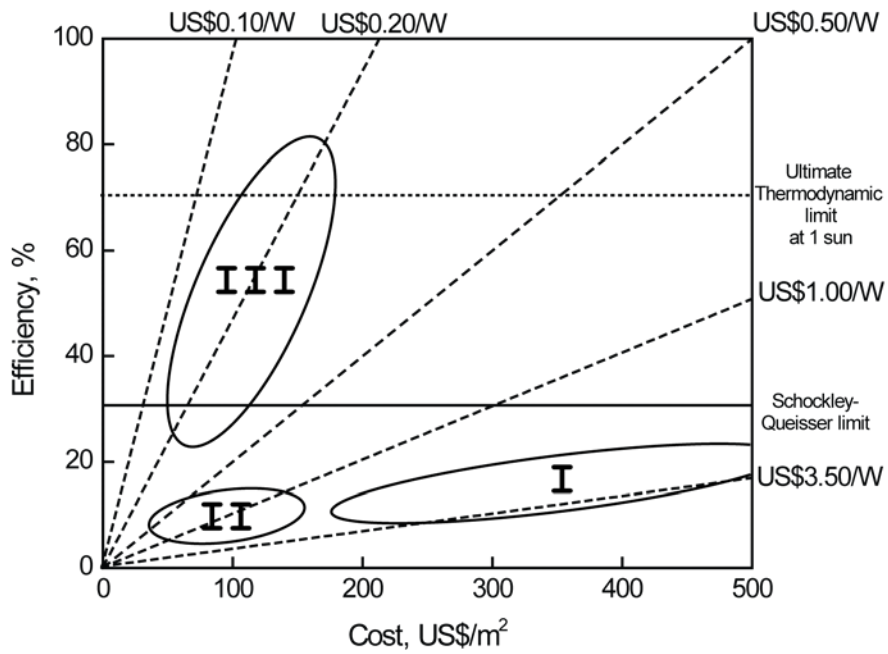
6 C.J. Brabec, J.A. Hauch, P. Schilinsky, C. Waldauf, Production aspects of organic photovoltaics and their impact on the commercialization of devices, MRS Bull. 30 (1) (2005) 50–52.

7 C. J. Brabec, Organic photovoltaics: technology and market, Sol. Energy Mater. Sol. Cells 83 (2-3) (2004) 273–292.

CHAPTER 2:
State-of-the-Art

The first OPV device was fabricated by Tang et. al. at Kodak and had a power conversion e_ciency (PCE) of 1.1 percent. This first device mimicked the structure of a traditional p–n junction. It was a bi–layer stack of copper phthalocyanine as the electron donor and a perylene tetracarboxylic derivative for the electron acceptor[8]. This initial design was only able to deliver a low PCE because the light–induced excited states (excitons) are tightly bound in organic molecules and can only separate at donor/acceptor interfaces. Typical exciton diffusion lengths are 5–25 nm. [9] [10] This small exciton diffusion length places a fundamental limit on the thickness that a material layer can have since light absorbed further from the interface will not result in charge separation and photocurrent.

Figure 1: PV Source Costs ($=Wp) as Function of Module Efficiency and Areal Cost



8 C. W. Tang, 2-layer organic photovoltaic cell, Appl. Phys. Lett. 48 (2) (1986) 183–185.

9 D.E. Markov, E. Amsterdam, P.W. M. Blom, A.B. Sieval, J.C. Hummelen, Accurate measurement of the exciton diffusion length in a conjugated polymer using a heterostructure with a side-chain cross-linked fullerene layer, J. Phys. Chem. A 109 (24) (2005) 5266–5274.

10 J. A. Barker, C. M. Ramsdale, N. C. Greenham, Modeling the currentvoltage characteristics of bilayer polymer photovoltaic devices, Phys. Rev. B 67 (7) (2003) 075205.

For PV to provide the full level of carbon–free energy required for electricity and fuel–solar power cost needs to be _2 cents/kWh ($0:40=*Wp* (Source: Green 2004).[11][6]

In the early 90's a new design for OPV active layers was developed called the bulk–heterojunction (BHJ). A BHJ consists of a mixture of donor and acceptor species in the same layer.[12] [13] The layer is formed by solution casting the donor–acceptor mixture from a common solvent. As the solvent rapidly evaporates, phase separation occurs between the two components. The degree of phase separation is determined by the solubility of the components in the solvent, the speed with which the film dries, and the mutual solubility of components in each other.[14] [15]

The new BHJ design has the major advantage that the distance between the donor and acceptor in the layer is reduced and the probability of charge separation approaches unity. However, the mixed film has reduced order, leading to reduced charge mobility, greater trap density, and island domains that do not have a charge transport pathway to either electrode. Until 2007, nearly all increases in OPV device PCE ultimately came about as a result improved BHJ layer morphology. For example, Shaheen et. al. found that using a solvent with improved mutual solubility for the two components could reduce the domain size of OC1C10-PPV / [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) mixtures.[16] Switching from the solvent toluene to chlorobenzene improved the PCE from 0.9 percent to 2.5 percent. Next it was discovered that the application of thermal treatment could be used to improve the hole mobility, increase crystallinity and increase efficiency in poly-3-hexylthiophene (P3HT)/PCBM mixtures.[17] [18] Simultaneously, it was found that the use of high–boiling–point solvents and long solvent–soaking times could optimize the morphology through self assembly.[19] [20] Finally, it was found

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11 M. A. Green, Third generation photovoltaics: advanced solar energy conversion, Springer-Verlag, 2003.

12 G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Polymer photovoltaic cells - enhanced efficiencies via a network of internal donoracceptor heterojunctions, Science 270 (5243),(1995) 1789–1791.

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15 J. Y. Kim, D. Frisbie, Correlation of phase behavior and charge transport in conjugated polymer/fullerene blends, J. Phys. Chem. C 112 (45) (2008) 17726–17736.

16 S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, 2.5% efficient organic plastic solar cells, Appl. Phys. Lett. 78 (6) (2001) 841–843.

17 F. Padinger, R. S. Rittberger, N. S. Sariciftci, Effects of postproduction treatment on plastic solar cells, Adv. Funct. Mater. 13 (1) (2003) 85–88.

18 W. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale controle of the interpenetrating network morphology, Adv. Funct. Mater. 15 (2005) 1617–1622.

19 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, High-efficiency solution

that the morphology could be optimized by using low–concentration additives[21] that could improve morphology either by selectively dissolving one the components[22] [23] or by causing rapid crystallization of the polymer during drying.[24] [25] All of the thermal, solvent, and additive techniques increase the PCE of a P3HT/PCBM device from ~1 percent to >4 percent.

An important research theme for the last 15 years has been the determination the mechanism for photocurrent production in a BHJ layer. Fig. 2a shows a diagram of a BHJ device based upon the commonly used mixture P3HT/PCBM. The mechanism for photocurrent production is depicted in Fig. 2b. Photons with energy above the optical band gap (E_g) are absorbed in the active layer by both the donor and acceptor materials, but since the donor polymer has a much larger absorption coefficient, the polymer typically absorbs the majority of the light. The absorbed photons form excitons, which for the purpose of this discussion are charge–separated excited states where both charges exist on the same species or polymer domain. In a BHJ, the exciton has a high probability of diffusing to a donor–acceptor interface and separating into a geminate charge pair. This geminate or bound pair, also known as a charge–transfer exciton, consists of a Coulombically bound hole on the donor and electron on the acceptor. The bound charge pair can be separated into free charges at room temperature when a sufficient electric field is applied. This built-in electric field is generated by sandwiching the BHJ layer between electrodes that have differing work functions. Finally, the free charges can hop from site–to–site under the influence of the built-in field until they reach their respective electrodes. Bound charge pairs can reform from free charges. Both bound pairs and free charges can recombine. Fig. 2b shows a generalized relaxation pathway. The kinetics of each process is strongly dependent on the morphology, donor/acceptor mixing ratio, electric field, and specific donor and acceptor species. Blom et. al. has written a detailed review of these mechanisms.[26]

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20 G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, Solvent annealing effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes, Adv. Funct. Mater. 17 (10) (2007) 1636–1644.

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22 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols, Nat. Mater. 6 (7) (2007) 497–500.

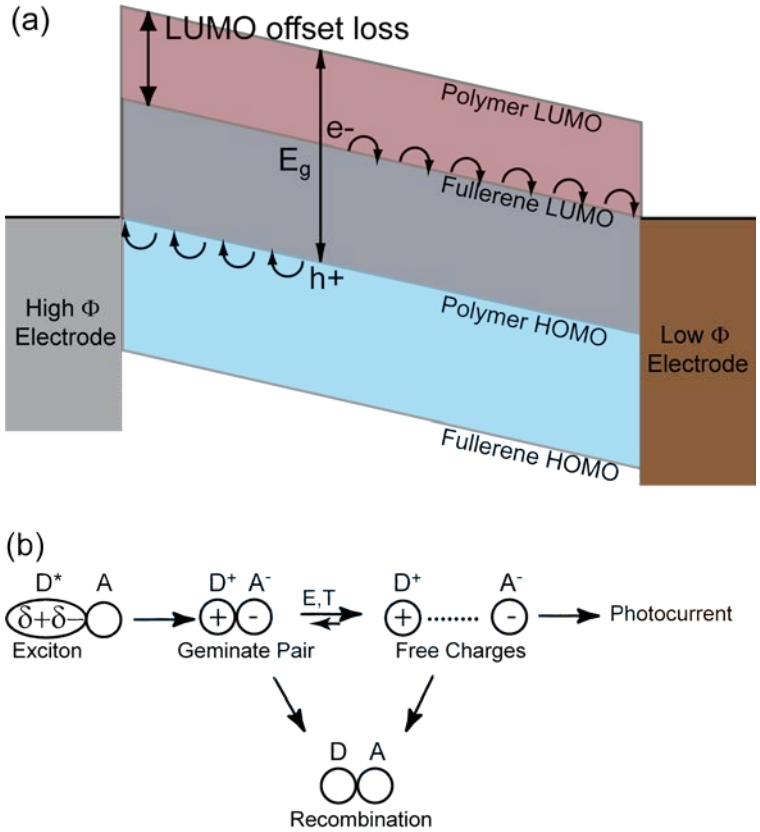
23 J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, A. J. Heeger, Processing additives for improved efficiency from bulk heterojunction solar cells, J. Am. Chem. Soc. 130 (11) (2008) 3619–3623.

24 A. J. Moul´e, K. Meerholz, Controlling morpholopy in polymer-fullerene mixtures, Adv. Mater. 20 (2) (2008) 240–245.

25 A. J. Moul´e, K. Meerholz, Morphology control in solution-processed bulk-heterojunction solar cell mixtures, Adv. Funct. Mater. 19 (2009) 3028–3036.

26 P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster, D. E. Markov, Device physics of polymer: fullerene bulk heterojunction solar cells, Adv. Mater. 19 (12) (2007) 1551–1566.

Figure 2: (a) Energy Level Diagram for an Organic Bulk Heterojunction PV Device under Short Circuit Conditions. (b) Cartoon of the Charge–Generation Process: Exciton Formation, Dissociation into Geminate Pairs, and Separation of the Geminate Pairs into Free Charges under the Influence of the Electric Field and Temperature to Produce Photocurrent



Geminate pairs and free charges can recombine to form neutral species.(Source Moule 2008)[27]

Since 2007, a number of new record efficiencies have been reported that can be directly attributed to improved synthetic design of either the donor or acceptor. Referring to Fig. 2a, three successful synthetic strategies can be identified. First, the short circuit current density (J_{sc}) can be increased by lowering the E_g and maintaining the polymer HOMO — fullerene LUMO spacing. The second possibility is to increase the open circuit voltage V_{oc} by maintaining the E_g but shifting the both the HOMO and LUMO of the polymer down in energy.[28][26] This shift will have the effect of lowering the energy loss labeled LUMO offset loss in the figure. The third possibility is to increase the V_{oc} while maintaining the E_g by raising the LUMO level

27 A. J. Moul´e, K. Meerholz, Intensity-dependent photocurrent generation at the anode in bulk-heterojunction solar cells, Applied Physics B: Lasers and Optics 92 (2) (2008) 209–218.

28 F. B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W. J. H. Verhees, J. M. Kroon, J. C. Hummelen, Increasing the open circuit voltage of bulkheterojunction solar cells by raising the lumo level of the acceptor, Org. Lett. 9 (4) (2007) 551–554.

of the fullerene. Two articles have predicted that these combined adjustments can yield power e_ciencies of over 10 percent.[29] [30]

A series of new co–polymer donors have been synthesized that use alternating electron rich and electron poor monomers. These so–called push–pull polymers have considerably smaller E_g than the homopolymers. Record efficiencies of 5.4 percent[31], 5.4 percent[32], 6.4 percent[33], and 7.9 percent[34] have been reported. All of the published results used various new push–pull polymers to achieve high efficiencies. References [160] and[35] detail the synthesis and design of new donor polymers for OPV. Fullerene–based acceptors have also recently been designed that increase the V_{oc} of the OPV devices by adjusting up the LUMO level of the acceptor. A bis–aduct of PCBM has been found to increase the V_{oc} by 0.15 V compared to the mono–aduct.[36] [37] Another acceptor, 1-(3-hexoxycarbonyl)propyl-1-phenyl-[6,6]-Lu3N@C81 (Lu3N@–PCBH) uses a C80 fullerene stabilized by a Lu3N cluster and is solubilized by a similar adduct to PCBM. Lu3N@– PCBH yields an increase in the V_{oc} of 0.2 V compared with PCBM.[38] [39] No work has yet appeared that uses both the new donors and acceptors together.

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29 L. J. A. Koster, V. D. Mihailetchi, P. W. M. Blom, Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells, Appl. Phys. Lett. 88 (9) (2006) 093511.

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31 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols, Nat. Mater. 6 (7) (2007) 497–500.

32 http://www.plextronics.com/press detail.aspx?PressReleaseID=7&archive=y, Press release: Plextronics' organic solar cell technology breaks world record:nrel certifies cell efficiency, website (August 2007).

33 http://www.konarka.com/index.php/site/pressreleasedetail/national energy renewable laboratory nrel certifies konarkas photovoltaics, Press release: National renewable energy laboratory (nrel) certifies konarkas photovoltaic solar cells at 6.4

34 http://www.pv tech.org/news/ a/solarmer breaks organic solar pv cell conversion e_ciency record hits nre/, Press release: Solamer breaks organic solar pv cell conversion efficiency record, hits nrel-certification, website (December 2009).

35 B. C. Thompson, J. M. J. Frechet, Organic photovoltaics – polymerfullerene composite solar cells, Angew. Chem. Int. Ed. 47 (1) (2008) 58–77.

36 G.-J. A. H. W. F. B. K. S. C. V. J. C. H. P. W. M. B. Martijn Lenes, Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells, Adv. Mater. 20 (11) (2008) 2116–2119.

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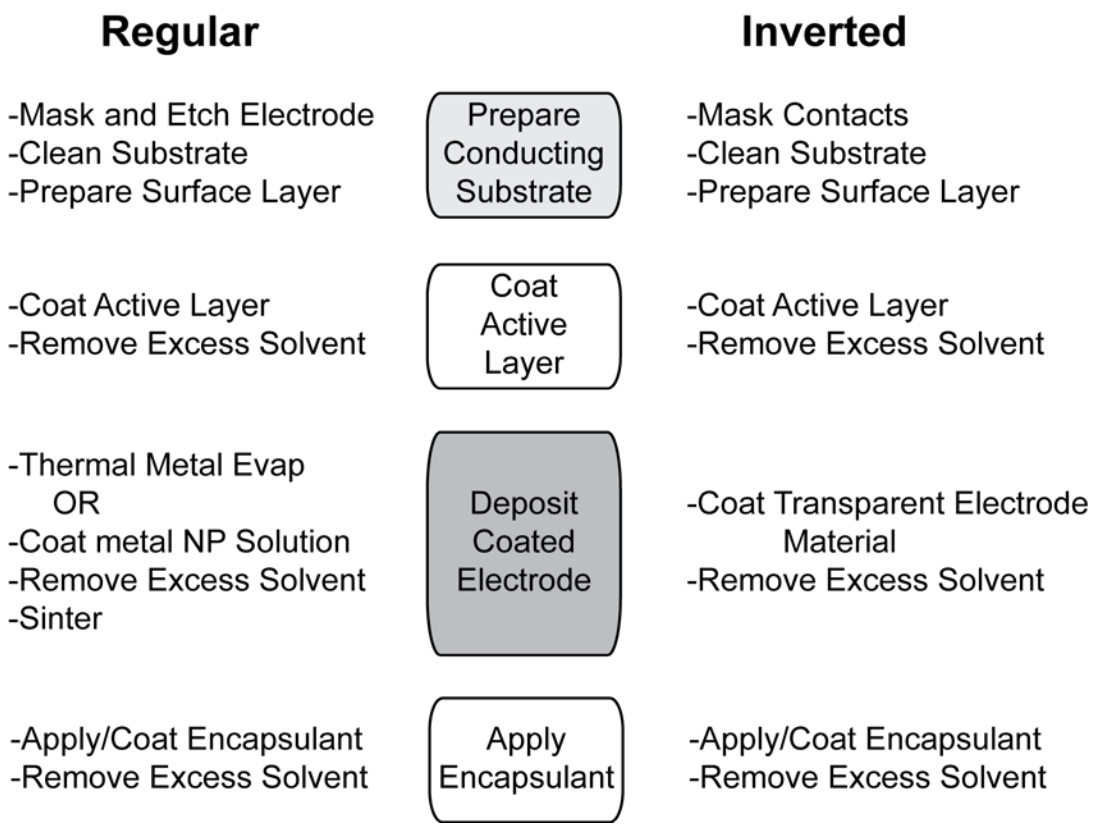
The increases in PCE over the last decade came about as a result of improved synthesis, morphology control, and a better understanding of the device physics. The synthesis achievements were due to increased understanding of how to synthesize lowband-gap polymers and how to control the energy levels of the polymers with respect to PCBM. However, morphology studies have been mostly performed on OC1C10-PPV/PCBM and P3HT/PCBM mixtures. The domain size, crystalline, and curing method (temperature, solvent soak, or solvent additive) can now be chosen for these mixtures. A better understanding of optical and electrical loss mechanisms has also been gained for these mixtures. But, there is still quite a lot of academic research that needs to be performed in all three of these areas. Hopefully, the scientific community will have increased access to the new low-band-gap co-polymers for morphology and device physics studies in the near future.

CHAPTER 3:
From Lab Bench to Rooftop

In a research lab, OPV devices are fabricated in miniature to conserve materials and to allow researchers to test the greatest number of experimental possibilities. This experimental flexibility leads to the practical difficulty that experimental results and efficiency records are achieved under conditions that are not scalable to or practical for mass production of large area OPV devices. This section will address some of the issues related to scale-up.

Fabrication of an OPV device involves four broad sequential steps. First, a conducting substrate with an optimized work function and surface energy is created. Second, a BHJ layer is coated onto the substrate. Next a second electrode is deposited onto the BHJ layer. Finally, the device is encapsulated in a material that protects the active layers from exposure to H_2O, O_2, and UV irradiation (Fig. 3).

Figure 3: A Flow Chart that Shows the Four Sequential Steps Needed to Fabricate an Air–Stable



OPV device for both regular and inverted fabrication. As discussed in the introduction, in order for OPV to be a viable competitor against other technologies, it is necessary to produce OPV at minimal cost. The fabrication will be discussed assuming a reel–to-reel fabrication. OPV devices

can either be regular (ie holes move towards the substrate) or inverted (ie holes move away from the substrate). The direction of current flow is determined by the choice of electrode materials.

One of the requirements for reel-to-reel coating is that the substrate be flexible so that it can be pulled through the reels. Regular devices can be fabricated onto transparent plastic foils that have been coated with a transparent conducting oxide (TCO) such as ITO or SnO2:F. The first step for fabrication has been shaded in Fig. 3 because TCO materials are not flexible and will crack when drawn through bends with a low radius of curvature. Cracks in the TCO degrade electrical performance of a device significantly. The shading indicates that this topic requires considerable innovation. An inverted device can either be coated onto a metal foil or onto a preformed metal part. Preparation of the substrate electrode requires similar steps for both device types. First the electrode must be either etched into the required shape or a resistive coating must be applied to prevent shorts where the electrodes will be externally contacted. Then the substrate material must be extensively cleaned and the electrode materials coated with a layer of material that sets the work function. PEDOT:PSS is commonly used on top of ITO for a hole contact for regular devices. TiO_x is a typical choice for an electron collecting material for an inverted device.[40]

The second step is coating of the active layer mixture. This step is performed identically for both device types. The only difference that could arrise in the film comes from possible differences in morphology. Since regular and inverted devices have differing electrodes the surface energies of the prepared substrates could be different. This difference in surface energy could lead to differing surface driven formation of morphology features. If the outer surface of the substrates has differing surface energies, the coating conditions must be adjusted to acheive similar layer thickness and dry morphology. For both device types, excess solvent must be driven from the BHJ film to ensure morphological stability.

Next comes the coated electrode. This step is marked in dark gray in Fig. 3 because this is the area that requires the most innovation for both device types. In the case of a regular device, a metal electrode must be deposited. A metal is always chosen for the back electrode material because it reflects transmitted light back through the active layer and thereby increases light absorption and photocurrent. Thermal evaporation of a metal is used in a research lab for electrode deposition. Thermal evaporation requires small device areas and high vacuum conditions that are not compatible with reel–to–reel fabrication. A solution method would be preferable. Low–temperature deposition of a transparent conducting electrode for an inverted device is even more diffcult because oxides and conducting polymers have lower conductivity and are more complex materials than metals. For both device types, heat treatments must remain below 200˚C to prevent damage to the BHJ material. No effective solution–coating method currently exists at low temperature deposition that provides conducting electrodes.

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40 C.Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S. A. Choulis, C. J. Brabec, Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact, Appl. Phys. Lett. 89 (23).

Finally, an encapsulant material must be applied that blocks O_2, H_2O, and UV radiation from the active layer material. The requirements of the encapsulant materials are that it be transparent, flexible, durable, impermeable, and low-cost. The deposition should also not destroy any of the layers already deposited and should not require curing temperatures above 200˚C. For this step, solution–based or lamination–based application of the encapsulant layer are preferable. Also for this step, the application should be identical for both device types.

3.1 Substrates

The prerequisite for an OPV substrate material is that it be highly conducting. As discussed above, the substrate can either be a metal or a transparent conductor. Research lab OPV devices are typically fabricated on indium–tin oxide (ITO) coated glass substrates that are cut and etched to a predetermined size and shape. For regular devices, polyethylene dioxythiophene polystyrenesulphonate (PEDOT-PSS) is spin coated to form the hole–collecting electrode. PEDOT:PSS makes a superior electrode to ITO because its work function is larger and it is selective to hole transport.[41][38] However, PEDOT:PSS cannot be used alone because the sheet resistance is too high without the ITO present. Cs2CO3[42] and NiO[43] have also been used as a hole collecting electrodes. For inverted devices a solgel of TiO2[44] , ZnO[45] or V2O5[46] is coated onto the ITO surface to make an electron selective contact. For both device types, transparent ITO coated polyethylene substrates (PET) can also be used as a substrate material. The PET substrate has the significant advantage that it is flexible, and so is compatible with a reel-to-reel coating technique. However, ITO coated onto PET has been shown to develop cracks upon bending that leads to significant reduction in the conductivity of the substrate.[47]

All TCO electrode materials are likely to be brittle and perform poorly after bending. For this reason, a number of groups are working on transparent electrode materials based on organic components. Single walled carbon nanotubes (CNT) have been studied for use as a transparent

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41 H. Frohne, S. E. Shaheen, C. J. Brabec, D. C. Muller, N. S. Sariciftci, K. Meerholz, Influence of the anodic work function on the performance of organic solar cells, ChemPhysChem 3 (9) (2002) 795–799.
42 G. Li, C.W. Chu, V. Shrotriya, J. Huang, Y. Yang, Efficient inverted polymer solar cells, Appl. Phys. Lett. 88 (25).
43 M. D. Irwin, B. Buchholz, A. W. Hains, R. P. H. Chang, T. J. Marks, ptype semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells, Proc. Natl. Acad. Sci., USA 105 (8) (2008) 2783–2787.
44 C.Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S. A. Choulis, C. J. Brabec, Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact, Appl. Phys. Lett. 89 (23).
45 M.S. White, D.C. Olson, S.E. Shaheen, N. Kopidakis, D.S. Ginley, Inverted bulk-heterojunction organic photovoltaic device using a solution derived ZnO underlayer, Appl. Phys. Lett. 89 (14).
46 G. Li, C.W. Chu, V. Shrotriya, J. Huang, Y. Yang, Efficient inverted polymer solar cells, Appl. Phys. Lett. 88 (25).
47 F. Krebs, Polymer Photovoltaics: A practical approach, SPIE press, 2008.

electrode material.[48] [49] However, CNTs are synthesized as a mixture of semiconducting and metallic tubes. Schottky contacts form at junctions between the semiconducting and metallic tubes that cause significant reductions in conductivity, resulting in high sheet resistance.[50] A second approach is to replace the TCO with a graphene–based composite.[51] [52] This approach leads to high sheet–resistance electrodes and is much too expensive with the current high price of graphene. A number of groups have used a doped conjugated polymer, such as highly doped PEDOT:PSS, to replace the TCO.[53] [54] [55] The conductivity of PEDOT:PSS is lower than that of most TCOs and so the resulting devices have reduced filling factor. Nevertheless, OPV devices with a PEDOT:PSS electrode based on P3HT/bis-PCBM has been reported with a PCE of 3.5 percent.[56] Another approach to making an electrode transparent is to fabricate a nanoscale metal mesh with most of the area being transparent. OPV devices have been fabricated based on Agnano wire meshes that show promising efficiency.[57] A recent article looked at the relationship between series resistance (R_s) that comes from the substrate itself and IV characteristics of OPV devices. They found that low R_s is critical for maintaining a high FF and PCE, especially as device area is increased.[58]

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48 Z. C. Wu, Z. H. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, A. G. Rinzler, Transparent, conductive carbon nanotube films, Science 305 (5688) (2004) 1273–1276.

49 M. W. Rowell, M. A. Topinka, M. D. McGehee, H. J. Prall, G. Dennler, N. S. Sariciftci, L. B. Hu, G. Gruner, Organic solar cells with carbon nanotube network electrodes, Appl. Phys.Lett. 88 (23).

50 M. A. Topinka, M. W. Rowell, D. Goldhaber-Gordon, M. D. McGehee, D. S. Hecht, G. Gruner, Charge transport in interpenetrating networks of semiconducting and metallic carbon nanotubes, Nano Lett. 9 (5) (2009) 1866–1871.

51 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruo_, Graphenebased composite materials, Nature 442 (7100) (2006) 282–286.

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55 S. K. Hau, H.-L. Yip, J. Zou, A. K. Y. Jen, Indium tin oxide-free semitransparent inverted polymer solar cells using conducting polymer as both bottom and top electrodes, Org. Electron. 10 (7) (2009) 1401–1407.

56 H. Do, M. Reinhard, H. Vogeler, A. Puetz, M. F. G. Klein, W. Schabel, A. Colsmann, U. Lemmer, Polymeric anodes from poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) for 3.5% efficient organic solar cells, Thin Solid Films 517 (20) (2009) 5900–5902.

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58 M. J. Harding, D. Poplavskyy, V.-E. Choong, F. So, A. J. Campbell, Variations in hole injection due to fast and slow interfacial traps in polymer light-emitting diodes with interlayers, Adv. Funct. Mater. 20 (1) (2010) 119–130.

In the introduction it was stressed that one major advantage of OPV technology is that it is compatible with flexible substrates. In fact, the coating of BHJ layers can conceivably be controlled better using a reel–to–reel coating technique rather than spin coating. This discussion of research into substrate materials reveals that all efficiency records have been recorded using ITO coated with PEDOT:PSS as the transparent electrode in spite of the fact that ITO has been widely predicted to be too expensive[59] and has been shown to perform very poorly in mechanical stress tests.[60] PEDOT:PSS is also not ideal for use in an OPV device because it is highly acidic[61] [62] and thought to be a source of degradation in the active layer.[63] It is therefore extremely important that a strong and dedicated research emphasis be placed on the development of new transparent electrode materials that are compatible with OPV fabrication conditions.

3.2 Coating

In a lab setting, BHJ layers are typically formed using spin coating. Spin coating is a batch coating method that requires that each individual small–area substrate be loaded and coated separately. The spin–coating technique does not effectively scale up to large–area coating. A more cost–effective alternative is to use flexible substrates that can be coated using a reel–to–reel technique in which the substrate is passed through a series of reels and the layers are sequentially coated using a compatible coating technique. Several groups have started working on reel–to–reel coating methods for OPVs. Several groups have developed an inkjet printing (Fig. 4a) techniques for P3HT/PCBM BHJ layers on regular electrodes that yielded power conversion efficiencies of over 3 percent.[64] [65] [66] The authors reported that the morphology formed from inkjet printing is distinctly different than from spin–coated or doctor–bladed layers.[67]

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59 F. Yang, S. R. Forrest, Organic solar cells using transparent sno2-f anodes, Adv. Mater. 18 (15) (2006) 2018–+.

60 F. Krebs, Polymer Photovoltaics: A practical approach, SPIE press, 2008.

61 K. W. Wong, H. L. Yip, K. Y. Luo, Y. Wong, L. W. M., K. H. Low, H. F. Chow, Z. Q. Gao, W. L. Yeung, C. C. Chang, Blocking reactions between indium-tin oxide and poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate) with a self-assembly monolayer, Appl. Phys. Lett. 80 (15) (2002) 2788–2790.

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This result suggests that the current practice of studying the morphology of BHJ devices fabricated from spin coating may yield scientific data that is not technically relevant for the coating techniques most likely to be used. Shaheen et. al. have used screen printing (Fig. 4b) to coat OC1C10-PPV/PCBM OPV devices.[68] Kim et. al. have used a brush coating technique to coat P3HT/PCBM layers. They found that the PCE is highly dependent upon the substrate temperature during coating. A high coating temperature led to phase separation on a larger length scale.[69] A likely coating technique to be used for industrial scale–up of BHJ printing onto flexible substrates is slot–die coating (Fig. 4d).[70] [71] [72] Slot–die coating has the advantages of being amenable to reelto-reel printing, it is a metered coating technique, which means that no ink is lost, and either single or multiple layers can be coated.

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67 P. Schilinsky, C. Waldauf, C. Brabec, Performance analysis of printed bulk heterojunction solar cells, Adv. Funct. Mater. 16 (2006) 1669–1672.

68 S. E. Shaheen, R. Radspinner, N. Peyghambarian, G. E. Jabbour, Fabrication of bulk heterojunction plastic solar cells by screen printing, Appl. Phys. Lett. 79 (18) (2001) 2996–2998.

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70 F. C. Krebs, Fabrication and processing of polymer solar cells: A review of printing and coating techniques, Sol. Energy Mater. Sol. Cells 93 (4) (2009) 394–412.

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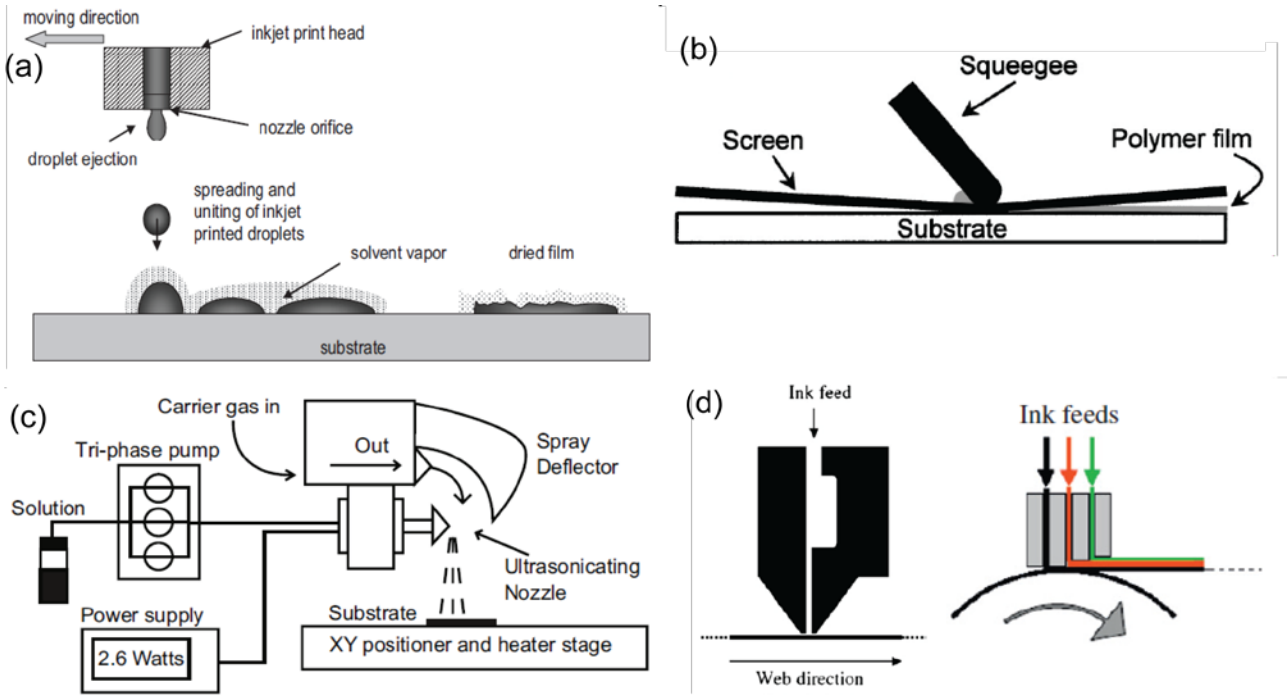
Figure 4: Schematic Diagrams of (a) Inkjet Printing[73], (b) Screen Printing[74], (c) Spray Coating[75], and (d) Slot Die Coater Heads for Single and Multiple Layers[76]



Reel–to–reel coating methods are useful for coating onto flexible substrates, which should be an advantage of OPV technology since the active layer film is highly flexible. However, for many applications a flexible substrate is not suitable. For example if an OPV coating is to be used as a photovoltaic replacement for automobile paint, the BHJ layer would have to be coated onto the ridged and curved pieces of an auto body. For this application, a spray coating (Fig. 4c) technique is more appropriate. Several groups have spray coated OPV devices onto glass/ITO substrates and achieved PCEs of over 3 percent.[77] [78] [79] [80] [81] [82] [83] The main issues for spray–

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coating appear to be formation of sufficiency small droplets, wetting of the substrate, film drying rate, containing airborne solvent, and reducing the surface tension of the ink.

3.3 Coated Electrodes

For a functional OPV device, the active OPV layer is sandwiched between two electrodes and one of the electrodes must be transparent. These requirements mean that the second electrode must be deposited on top of the active OPV layer. Since the active layer is made from a polymer, the deposition technique must be compatible with low temperatures, to prevent damage, and/or hydrophilic solvents that will not redissolve the polymer layer. The need for a low–temperature deposition technique means that sputtering cannot be used on the polymer because the sputtered material will burn the organic upon deposition. However, if an oxide layer is deposited using a sol–gel, then a metal can be sputtered on top. In a research lab, the back electrode for a regular device is typically deposited by a metal evaporation source in high vacuum conditions. The metal must be evaporated at a rate < 1 nm/s or the polymer can be burned.[84] Evaporation requires a vacuum source and is time consuming, which makes it a poor technique choice for high–speed and low–cost production of OPV devices. Ideally, a solution processing method should exist for the deposition of metal electrodes. The current best alternative to evaporation is to coat a suspension of metal nanoparticles (commercially available) and create a low conductivity porous electrode. Again because of the restriction that temperatures over 200˚C cannot be used to avoid damage to the OPV layer, the metal particle layer cannot be sintered to increase the connectivity between the particles. A more attractive solution for metal electrode deposition currently does not exist. One interesting advantage of

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Electron. 10 (4) (2009) 587–593.

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81 D. Vak, S.-S. Kim, J. Jo, S.-H. Oh, S.-I. Na, J. Kim, D.-Y. Kim, Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation, Appl. Phys. Lett. 91 (8) (2007) 081102.

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the deposition of metal nanoparticles for electrodes is that the deposition technique is compatible with spray–coating conditions.[85]

Deposition of transparent electrodes for inverted devices is more difficult. TCO materials such as ITO, ZnO, and SnO2:F can all be deposited using sputtering techniques, but as discussed above, these techniques can burn the underlying OPV material. In addition, sputtering requires a vacuum and cannot be performed continuously in a reel–to–reel deposition. Sol–gel methods exist to deposit some oxides, such as TiO2, but the resulting layers have much too high a sheet resistance to be used as the electrode material. In the section on substrates, several alternatives for deposition of transparent electrodes, including CNTs, highly doped conjugated polymers, and Ag nanowire meshes are identified. Deposition of the top electrode is more difficult because not only must the requirements of transparency and conductivity be met for the top electrode but the material must also be prepared in a form that can easily be coated from a solution in a reel–to–reel fabrication onto a low surface energy film. These very high requirements make the development of a coatable transparent electrode material the most difficult challenge for mass production of OPV devices. If such an electrode material can be developed, it will open the way for the development of truly transformational technologies such as photovoltaic car and building paints.

3.4 Encapsulating Materials

Most research on OPV devices is performed in N2 gloveboxes. It is well known that OPV devices will degrade quickly on exposure to air. The mechanisms for degradation follow three known pathways. First, the metal electrode is typically a low work–function metal that oxidizes on exposure to O2 or H2O.[86] [87] Second, if O2 is present in the active layer, it can be photo excited to singlet oxygen (O2*) which reacts with and bleaches the polymer. Third, upon exposure to long–term heating, the active layer can phase separate.[88] Both of the first two degradation mechanisms can be avoided if the O2 and H2O levels can be kept sufficiently low. However, the sensitivity of organic electronic materials to O2 is very high. O2 levels in the active layer must be kept four orders–of–magnitude lower than can be attained using typical food packaging encapsulants.[89] Several groups have focused research efforts on creating solution–processable transparent encapsulant barriers that are based on a mixture of clay pellets

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and polymers.[90] Several groups have also published results that show OPV device lifetimes greater than several thousand hours, but unfortunately the identity of the encapsulant material is usually not disclosed.[91] [92] [93] The study of lifetime in OPV devices is particularly difficult because devices are very complicated, layered, and the defect states are below the limit of detection for most optical detection techniques. There is some evidence that defect states form at the metal electrode surface even in dark oxidant–free conditions.[94] In conclusion, it appears that encapsulant materials suitable for OPV applications have been developed though the identity of the materials is intellectual property. On the other hand there is not enough known about the basic mechanisms behind OPV device degradation. This author recommends much more basic research on the applied problem of lifetime enhancement in OPV devices with a particular emphasis on studying interfaces between layers and developing measurement techniques that are sensitive to interface states at buried interfaces.

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92 J. A. Houch, P. Schilinsky, S. A. Choulis, S. Rajoelson, C. J. Brabec, The impact of water vapor transmission rate on the lifetime of flexible poly solar cells, Appl. Phys. Lett. 93 (2008) 103306.

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CHAPTER 4: Conclusion

Organic photovoltaics is a fascinating subject to study. It is necessary to be familiar with optical absorption processes, charge transport, polymer morphology, recombination kinetics, the relationship between polymer structure and electronic and optical properties, the interaction between metal and organic layers, and a host of other interesting basic science themes. The increase in the power conversion efficiency of organic photovoltaics from < 2 percent to 7.9 percent in eight years is mostly due to intense and focused academic research on the basic science issues surrounding every aspect of this device type.

In the past 2–3 years several companies have started to produce OPV materials and have reported record PCEs that cannot be matched by academic groups. This is, however, not the right time for reduced governmental support of academic research in this area. In fact much more research is needed. This review article has focused on the scale-up of OPV to a reel–to–reel solution–processed and mass–produced product. Almost the entire article stresses that research must still be done on flexible transparent electrodes, solution–processable electrodes (metal or transparent), developing reel–to–reel and spray coating methods, studying polymer morphology that results from the new coating methods, developing effective transparent O2 and H2O barrier materials, and learning to make all of these technologies work together.

4.1 Benefits

Large– scale production and distribution of low-cost OPV modules can play an important role in greenhouse gas reduction and meeting global energy demands. These goals are urgent and need to be addressed by increased funding of basic and applied research in this area.