

Stability/Degradation of Polymer solar cells- A review

Ashwin B. Badhiye¹, Mohsin S. Pothiyawala²

^{1,2} G. H. Raison College of Engineering, Nagpur, India

Abstract- Polymer and organic solar cells degrade during illumination and in the dark. This is in contrast to photovoltaics based on inorganic semiconductors such as silicon. Long operational lifetimes of solar cell devices are required in real-life application and the understanding and alleviation of the degradation phenomena are a prerequisite for successful application of this new and promising technology. In this review, the current understanding of stability/degradation in organic and polymer solar cell devices is presented and the methods for studying and elucidating degradation are discussed. Methods for enhancing the stability through the choice of better active materials, encapsulation, application of getter materials and UV-filters are also discussed.

Keywords- alkythiophenes, unencapsulated, photooxidation, photovoltaics, polymer

I. INTRODUCTION

The development of polymer solar cells has become an active field of research in recent years. Inorganic thin film silicon solar cells using nano-crystalline and amorphous silicon have already achieved reasonable power conversion efficiency of 12-15% which are somewhat lower than that of thick crystalline silicon solar cells (22-24%). Both periodic photonic-plasmonic and random textured back reflectors have enhanced the conversion efficiencies and photo-current by increasing the photon path length and utilizing advanced photon management scheme.²⁻¹⁰ Alternate inorganic solar cell materials are cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) which have achieved 15-20% power conversion efficiency. However, fundamental limitation of such inorganic solar cells is the limited availability of the active layer material. Also toxicity is a major concern for materials like CdTe. Organic conjugated polymers have an advantage over its inorganic counterparts in its flexibility in material properties. By carefully changing certain elements and side groups in the polymer, it is possible to change the fundamental property of the polymer namely the band gap, electron density, electron affinity and ionization potential. The change in the position of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) can have tremendous influence on the efficient charge generation and charge separation at the bulk hetero junction interface. The use of bulk industrial production techniques such as roll

to roll fabrication, doctor's blading, spray coating, inkjet printing have made it possible to produce organic solar cells in automated manufacturing unit. It was experimentally observed that prolonged light exposure can create defect states (subband gap states) inside the polymer, which can increase the rate of monomolecular (Shockley-Read-Hall) SRH recombination because those states can act as a recombination centers. Some work suggested possible evolution of trap states in the electron acceptor phase may induce loss in photo current. In a very recent work Street et al had also proved that light induced creation of recombination centers is a dominant source of loss mechanism in photo-3 degradation dynamics. Further, authors have argued that cession of C-H bond present in alkyl side chain of polymer and subsequent migration of H atom along the backbone could be a probable cause of x-ray/white light induced creation of energetic defect states at the mid-gap in the interface of bulk hetero-junction. The role of electron acceptor was investigated in the photooxidation behavior of organic solar cells in another study. We studied the effect of photo degradation on different electrical parameters that govern the power conversion efficiency of the polymer based solar cell. It was found that solar cell's open circuit voltage (Voc) as well as short circuit current (Isc) are directly affected by prolonged light soaking. The loss in photovoltaic performances can be directly attributed to the increased amount of trap assisted (SRH) recombination through the mid gap states at donor-acceptor interface. We have studied systematically the effect of different inter-layers on the photo-degradation of the organic solar cell. We identified functional relationships of induced defect density with various doses of exposure of full spectrum white light. The DOS (density of states) of BHJ solar cell were measured in-situ, as a function of exposure time to study the dynamics of change in defects in the device with exposure time. We investigated the effect of post-production annealing as a method of complete device performance recovery and its implication on the device performance as well as change in fundamental properties. We showed that it is difficult to see the changes in the induced defect states by post degradation annealing because of diffusion of metal contacts into the active layer and subsequent formation of recombination centers. We showed that by obtaining a thermally stable anode, we can see the complete recovery of device performance by post production annealing.

II. MOISTURE INDUCED DEGRADATION

Moisture is one of the most important degradation constituents that reduces PCE of unencapsulated polymer based solar cells. Krebs et al⁴⁶ in their paper suggested that the water molecule diffuses through the Al cathode. It was suggested that the water molecules are absorbed into the Al cathode and it then diffuses further towards the ITO layer and through all other interfacial layer leading to the degradation of all interfacial layers.⁴⁶ Water induced degradation was termed as homogeneous degradation compared to inhomogeneous degradation through oxygen. It was further suggested that the presence of molecular oxygen and light accelerates the water induced degradation. Under illumination, the active layer of the solar cell undergoes different photo chemical reaction between constituent of the device and the atmospheric agents.

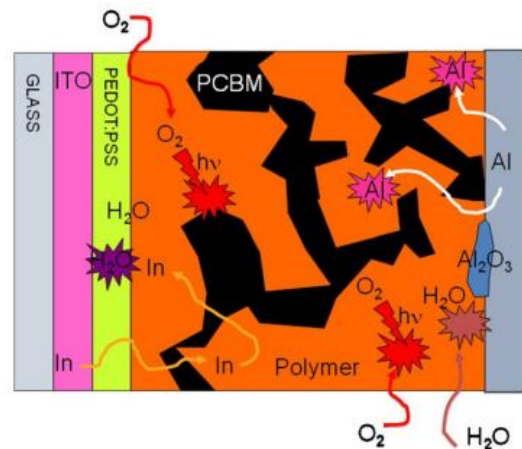


Figure 3. Different degradation pathways depicted –attacking different parts of solar cell.

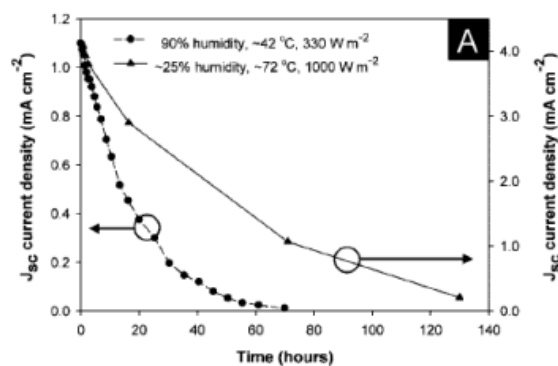


Figure 1. Drop in Jsc under different humidity and different light intensity exposure to MDMOPPV-PCBM cell.

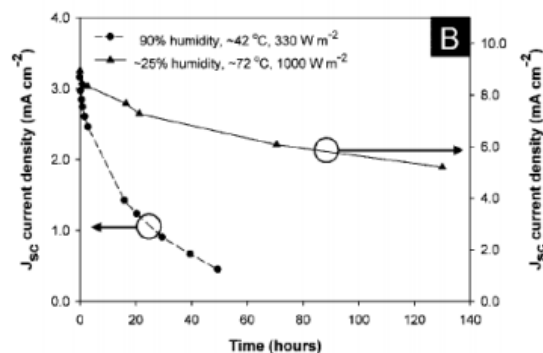


Figure 2. Drop in Jsc under different humidity and different light intensity exposure to P3HT:PCBM cell

The figure shows different degradation pathways. In the process of chemical degradation the diffusion of both molecular oxygen and water are the important source of degradation. It also suggested that there can be different pathways of diffusion of oxygen, water, aluminum or indium into the active layer which can initiate degradation in OPV. It was further emphasized that oxygen can be activated by UV illumination in the presence of some organic molecules, which lead to the formation of peroxide or superoxide compounds that further aggressively attack and degrade the active layers. Different polymer are prone to such chemical degradation at different rates. For example, the PPV based polymer such as MDMOPPV is susceptible to such active layer degradation. Diffusion of molecular oxygen and moisture were thought to be initiated through the microscopic pinholes formed on the aluminum cathode. The following high resolution secondary electron microscope (SEM) image of the aluminum cathode shows big crater like structure which substantiates the possibility of having microscopic pinholes.⁴⁶ Another entrance route for these molecules could be the aluminum grain boundaries at the surface of the aluminum cathode.

III. OXYGEN DOPING AND RELATED DEGRADATION

Oxygen is considered to be an important element that was considered responsible for the degradation in polymer based solar cells. In this section we will review the degradation pathways initiated by oxygen. Significant research was already done on assessing how oxygen took an active part in degrading the polymer active material and hence reducing the power conversion efficiency (PCE) of polymer based solar cells. One of the pioneering researcher in the field of degradation study of organic polymer based solar cells is Dr F Krebs who published a large amount of research on studying

the effect of oxygen exposure on the different polymer based solar cells and their subsequent degradation pathways.

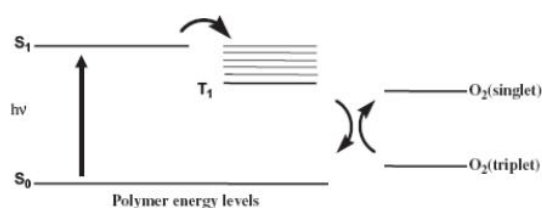


Figure 4. Formation of triplet state due to the presence of oxygen.

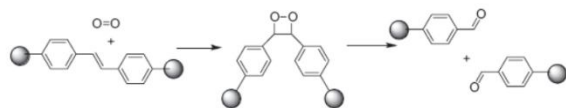


Figure 5. Breaking of backbone in the presence of light and oxygen.

In the figure 2.2 (a) it was described how the electronically excited triplet oxygen reacts with the PPV polymer. The polymer first reaches an excited state S1 followed by a transition to a triplet state T1. In the T1 state the polymer can transfer the excitation to the adsorbed oxygen. This results in the formation of singlet excited state. The electron donation from polymer excited state to the oxygen results in the reaction of the polymer chain with the singlet oxygen and form- 10 ing an intermediate di-oxytane and finally a rupture of the polymer chain. The final product can further react with oxygen. Dam et al found that oxygen initiated reactions with polymer depends on nature of reactive groups⁴⁸. Electron donating groups enhance the rate of reaction while the electron withdrawing groups retard the reaction rate.

The polymer P3HT does react with oxygen at the temperature as low as -50 C. It was observed that thiophene based polymer such as poly(3-alkylthiophenes) form charge transfer complexes with oxygen. The resulting negative and positive radical species can be detected by electron spin resonance. These authors concluded from their finding that , oxidation of P3HT results in the loss of absorption in the P3HT absorption band and lead to the further reduction in both short-circuit current and open circuit voltage. In the same paper by Jorgensen et al, the authors argued that the oxygen exposure not only degrades the polymer intrinsically but also reacts with the calcium used for making cathode contact.⁴⁸ It forms Calcium oxide at the cathode –polymer interface resulting in higher series resistance and lowering of the fill factor. It was suggested that further thermal annealing steps can be applied to heal the degradation in the active material but formation of the CaO interfacial oxide is irreversible.

IV. LIGHT INDUCED DEGRADATION-PHOTO OXIDATION

In the previous sections 2.1 and 2.2 we briefly surveyed that molecular oxygen species can diffuse and react with the active layer. However it was further emphasized that the oxygen reactivity with different polymer systems become accelerated in the presence of light. Most of the scientific community termed it as a photo oxidation effect. In this section we will discuss in detail, the effect of photo induced changes in different polymer system. Photo induced degradation of both inorganic as well as organic material is a widely studied phenomenon. Many groups have already studied these phenomena in great detail. In a-Si: H the effect of light soaking was first demonstrated by David L Staebler and C. R. Wronski in 1976. They showed that both dark and photo conductivity of the hydrogenated amorphous silicon tend to decrease by prolonged light soaking. However it is possible to reverse the StaeblerWronski effect by thermally treating the solar cell devices by 160oC-200oC. Physically prolonged light soaking creates dangling bonds, resulting in mid-gap defect states which were considered responsible for performance drop in amorphous silicon solar cells. In one of the earliest models, light soaking breaks the weak Si-Si bond and then a neighboring H atom moves to make a bond with of the Si atoms resulting dangling bonds that have mid energy defect states.⁸⁵ Other models describe the rupture of Si-H bonds and formation of Si-dangling bond accompanied by Si:H complexes. Some other theory suggests that the rupture of Si-Si bonds are followed by the diffusion of strained species in the network and which lead to the formation of dangling bonds. Similarly several groups in last decade had investigated the mechanism of photo induced changes in the polymer based solar cells. A Rivaton et al ⁵⁸ conducted studies on the photo degradation of several polymer system based solar cells. They conducted studies on MDMO –PPV films as well as P3HT film with their corresponding bulk hetero-junction with PC60BM fullerene.

V. OTHER STABILITY RELATED ISSUES

Metal electrode This reactivity between the aluminum metal and the organic material has been recognized for a long time in organic chemistry, where such reactions have been used for reduction via electron transfer to organic compounds. Lo'gdlund et al proposed the direct interaction between the aluminum metal and polymer (PPV based materials) resulting in direct formation of Al-C bond. Aluminum is attractive metal to utilize because of its low work function which makes it useful as the negative electrode material in solar cells. The organo-aluminum compounds are highly reactive species that will react with any proton donors

present like oxygen in the atmosphere. One such proton donor could have traces of water introduced in the production of the device e.g. from PEDOT:PSS. The end result would be the reduction of the vinylene groups with a loss of conjugation in the polymer. The calcium electrode can react with water under room temperature. However calcium can't react with molecular oxygen under inert atmosphere. It was argued that calcium can also react with the organic compound and thus form C-Ca bond that can further react with oxygen in a similar way that oxygen reacts with the organic- aluminum compound. Different fullerene molecules also have the tendency to react with aluminum metal because of the high electron affinity of aluminum. C60 reacts with alkali metals to form compounds such as K3C60 where the alkali atom resides within the fullerene cage. A similar reaction could be envisaged at the interface between PCBM and the aluminum electrode though this has not yet been demonstrated.

VI. CONCLUSION

The field of polymer solar cells undergoes a rapid development where most of the research effort has been placed on developing devices with an improved efficiency. An equally important area that has received less attention is to extend the rather poor stability seen in the initial devices. Some progress has been made as detailed above. Polymer solar cells are complicated multilayer structures where each component may fail for different reasons and layers may even interact chemically and physically in ways that may cause degradation. Understanding is far from complete, but some main contributors to the degradation mechanisms have been pin pointed. Oxygen from the atmosphere will oxidize the organic layer, especially when the device is illuminated. This may seem to be a paradox: solar cells that degrade when exposed to light! Fortunately, newer materials such as P3HT and better P3CT are less prone to this degradation pathway.

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