Abstract

Charge carrier transport within bulk heterojunction organic solar cells has been simulated with the goal of extending the insights gained to analysis of transport between organics and metal oxides. In turn, this information will be applied to the metal oxide/metal electrode interfaces. Recent discoveries have shown that optimizing interfaces between the various layers in organic solar cells serves to improve overall device power conversion efficiency. Metal oxides can be a beneficial component when included within devices as they can improve spectral absorption, facilitate carrier transport, and have unique energy bandgap properties that make conduction between cell layers more energetically favorable. With the knowledge gained thus far, our group has begun expanding our simulation methods as they apply to metal oxide/organic interfaces. The focus of this report is to describe current understanding of oxide/organic interfacial characteristics.

Introduction

Perhaps now, more than at any other time, scientific efforts are concentrated on discovering new sources of renewable energy and improving the alternative technologies currently available. Solar energy is a primary focus with the study of organics being relatively new compared to the more traditional, inorganic silicon-based cell devices. Organic solar cell (OSC) research continues to be an extremely active area of exploration both in academia and in industry. In a broader sense, renewable energy sources are considered a critical component of the current strategy to meet economic development, job creation, national security, and clean environment needs. Presently, OSCs are beginning to show promise as potentially low cost, easily-fabricated, and reliable energy sources that could see ubiquitous application on a world-wide scale.

Based on new insights and increased understanding of organic materials, device concepts, and organic physics, the quality and performance of OSCs continues to evolve at a rapid pace. Still, the energy conversion efficiencies needed to make organic photovoltaics viable commercially have yet to be realized. The highest power conversion efficiencies (PCE) achieved to date remain at approximately 5~6.5% while inorganic devices have efficiencies exceeding 15%\(^4,5\). There are several reasons why organic solar cell performance levels are still lacking and, ironically, many relate to the inherently poor electrical characteristics found with the organic polymers used in device fabrication\(^6,7,8\). Higher exciton binding energies ranging from 0.2~0.5 meV, charge carrier mobilities less than \(10^{-2}\) \(\text{cm}^2/\text{V.s}\), and extremely short exciton diffusion lengths between 5~20 nm are obstacles that must be overcome if OSCs are to be made practically and commercially viable\(^10,11,12,13,14\).

In recent years, much has been learned regarding the mechanics behind charge transport between organic donor polymers/acceptor fullerenes that are mixed together in a bulk heterojunction (BHJ) configuration\(^1,2,3\). The close proximity and large mutual interfacial areas of the nanoscale constituents promotes efficient dissociation of excitons approaching 100\%\(^15\). However, this excellent internal quantum efficiency (IQE) is not the only driving force behind attaining high power conversion efficiencies. The charge carriers resulting from dissociated excitons must be efficiently collected at the device electrodes in order to be useful in the form of electricity. A number of factors impede this process including high electrical resistance at the electrode interfaces, and geminate and bimolecular recombination at the polymer/fullerene interfaces and within the bulk of the active layer, respectively. Our group has developed a modeling and simulation tool that allows for the analysis of several solar cell characteristics including charge carrier mobilities, recombination and dissociation probabilities, current densities, and device voltages\(^16,17,18\). Simulation results show that organic active layer thickness and the ratio of
electron/hole charge carrier mobilities are critical factors impacting efficiency.

Discussion

A relatively new approach to alleviating the aforementioned technical problems involves the inclusion of n- and p-type metal oxide semiconductors in device fabrication. These materials can be used in several ways to improve charge carrier conduction to both the anode and cathode electrodes in an OSC. Metal oxides have been used as electron/hole blocking layers (EBL/HBL), as transport layers, and even as “optical spacers” between electrodes/active layers where they can improve absorption and ultimately increase short circuit current densities (J_{sc}), fill factors (FF), and ultimately, power conversion efficiencies. The concept of implementing so-called hybrid organic-inorganic solar cells is gaining widespread interest, but the technical challenges in doing so are still many. For example, metal oxides and organic materials have dielectric constants that differ greatly and this could lead to a build up of charge carriers at the interfaces\(^ {19} \). This would impact device series (R_S) and parallel or shunt (R_SH) resistances that, in turn, have a direct influence on fill factor. The interrelationships between R_S, R_SH, current density, bias voltage, and FF can be seen in Figure 1.

![Figure 1](image.png)

**Figure 1.** (a) FF, (b) schematic of a solar cell, (c) series resistance, and (d) parallel resistance\(^ {20} \).

Figure 1 (a) shows the variables that determine fill factor in a solar cell. J_{max} and V_{max} are the current density and voltage bias measured at the maximum value (knee of the curve) of the J-V graph. J_{sc} and V_{oc} represent the short circuit current density and open circuit voltage, respectively. It is the ratio of the product of J_{max} and V_{max} to the product of J_{sc} and V_{oc} that defines FF. Figure 1 (b) shows a schematic representation of a solar cell. Ideally, R_S would approach a value of zero ohms while R_SH would be infinite. The diode represents the organic active layer which is the source of the charge carriers. In the representation of a J-V curve shown in the fourth quadrant (Figure 1 (c) and (d)), the inverse slope taken at the areas of the curves shown gives the values for R_S and R_SH. The series resistance is also impacted by such factors as the morphology, intrinsic resistance, and thickness of the organic active layer while shunt resistance is subject additionally to the affects of the type and degree of active layer defects and impurities that cause carrier recombination and leakage current\(^ {20} \).

It has long been known that surface modification of the transparent conducting electrode (typically indium tin oxide (ITO)) can improve OSC performance. However, despite being optically transparent and having high conductivity, ITO also has a low work function that must be overcome since a high work function anode is necessary to decrease series resistance\(^ {21,22} \). The most commonly-used material to address this problem is poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and it serves as a hole transporter between the organic active layer and the ITO anode\(^ {23} \). Still, PEDOT:PSS has some undesirable characteristics that make it less than ideal for this purpose including susceptibility to thermal degradation and a very low pH (~1) that makes it corrosive to the ITO electrode\(^ {23} \). As an alternative, surface modification of ITO can also be achieved through the use of metal oxides such as TiO_2, MoO_3, V_2O_5, NiO, and WO_3\(^ {24,25,26,27} \). Metal oxides offer a greater degree of controllability in that they can be used to “tune” the energy band alignment between the organic active layer and the oxide electrode material thereby minimizing charger transfer barriers across the interface\(^ {28} \). The focus of this paper is to highlight the properties and implementation strategies used when including metal oxide semiconductors in OSCs. The oxides to be addressed are TiO_2, WO_3, and MoO_3.

**Titanium Dioxide (TiO_2)**

Boucle, et al., described two approaches for incorporating TiO_2 in OSCs. In the first case, polymer is incorporated inside a rigid porous oxide
structure, and in the second oxide nanoparticles and polymer are mixed together and deposited as a solution to form the active layer. In both scenarios, the basic charge transfer mechanism is as shown in Figure 2.

![Figure 2](image)

Energy in the form of photons impinges on the donor polymer and produces excitons that diffuse to the polymer/metal oxide interface and dissociate into charge carriers. The metal oxide serves as an electron acceptor while the polymer transports the holes. Characteristics of the metal oxide acceptor include high electron mobility and affinity and mechanical and chemical stability. There are three basic structures normally used in hybrid organic-inorganic cells and two modes by which charges are transported to the electrodes. Structures can be 1) bilayer comprised of polymer on an inorganic layer, 2) porous where polymer is infiltrated inside the inorganic structure, and 3) blended where semiconductor nanocrystals are mixed with a polymer. In bilayer and porous structures, charges move to the electrodes via diffusion while excitons that dissociate into charge carriers in blends require a difference in the work functions of the electrodes to provide a bias for transport.

Metal oxide semiconductors are of particular interest in these structures because their morphologies can be controlled accurately using wet chemical synthesis. This allows the oxides to be fabricated having variable densities. In addition, other desirable properties of these materials include the capability for light-trapping, low cost, non-toxicity, and the fact they have been extensively studied. An example of a device taking advantage of variable-density metal oxide components is shown in Figure 3.

![Figure 3](image)

In this solar cell, a dense metal oxide acceptor layer is deposited on top of the ITO cathode. Next, this layer is covered by a mixture of porous metal oxide and organic polymer. Finally, additional polymer is deposited followed by a metal anode that serves as the hole collector. Note that the polarity of this cell is opposite to that normally observed in typical planar organic cells. See Figure 4 below for a comparison of device structures leading to opposite polarities.

![Figure 4](image)

This is possible due to the arrangement of the energy levels of each layered component. Figure 5 shows the energy level schematic of the inverted cell.
It’s important to note that ITO can be used as either a hole or electron collecting layer. This is due to its work function (4.5 to 4.7 eV) which lays between the HOMO and LUMO values of the organic layer. The dense TiO₂ layer serves as both an electron acceptor and a hole-blocking layer. This is key to improving cell performance since organic donor material that is in direct contact with the ITO will result in leakage current that decreases device fill factor. Note also that PEDOT:PSS is used between the polymer donor and the anode electrode. This layer serves as a hole acceptor and an electron blocking layer. Figure 6 shows the J-V characteristic curves for the device described in Figure 5 and for devices without the dense TiO₂ and “excess” spin-coated polymer layers.

In the cases where dense TiO₂ and spin-coated polymer are not included, it’s clear that FF has declined markedly. In each scenario, this is due to the lack of hole and electron blocking, respectively, where leakage current adversely impacts device performance. More specifically, these layers serve to prevent shunt pathways from forming (e.g., they increase RSH).

Devices designed based on a porous oxide/polymer structure have shown relatively poor efficiency values to date when compared with polymer/fullerene blends. Suggested reasons for this include inadequate polymer infiltration into the oxide material, excessive diffusion length between oxide and polymer, poor charge transport, and low photovoltage resulting from energy requirements needed to drive exciton dissociation. A number of factors must be addressed to minimize these problems including polymer infiltration, morphology of the oxide components, increase in charge separation efficiency, reduction of recombination, and increasing the rate of charge transport. Also, a known issue with nanocrystalline TiO₂ is charge trapping that limits carrier transport. Further complicating matters is that an increase in charge transport will probably result in a simultaneous increase in recombination.

A novel use of TiO₂ is as an optical spacer that increases efficiency in organic solar cells. Figure 7 shows schematic representations of both a conventional cell and a device incorporating an optical spacer. The diagrams show the amplitude of the electric field squared in each layer of the cells. The irradiance, I, is proportional to the square of the amplitude of the electric field and is given by the relationship

\[ I = \epsilon_0 c \langle E^2 \rangle_T \]

where \( \epsilon_0 \) is the permittivity of free space, c is the speed of light, \( \langle E^2 \rangle \) is the electric field, and the subscript T refers to the fact that irradiance corresponds to the average energy per unit area per unit time. The electric field, \( E \), is normally referred to as the optical field.
Of note is that in the device with the spacer, the magnitude of the irradiance is greater at every location throughout the entire thickness of the active layer compared to the conventional solar cell. This spatial redistribution of the irradiance will result in increased current density that subsequently improves energy conversion efficiency. As shown in Figure 8, devices containing an optical spacer show markedly improved $J_{SC}$.

In contrast, the conventional device shows the highest optical field amplitude close to the anode and a considerable portion of the active layer is not used for photogeneration of charges. This condition results in greater exciton generation and dissociation at this depth and leads to excess charge build up. Use of an optical spacer can improve device efficiency by up to 50% compared with that of a conventional solar cell.

**Tungsten Oxide (WO$_3$)**

Insertion of thermally-evaporated WO$_3$ films (5-30nm thick) between polymer/fullerene (P3HT:PC$_{60}$BM) and ITO conductive electrode layers has resulted in organic solar cells having efficiencies as high as 3.1%\cite{27}. Correspondingly, fill factors of 0.70 were achieved and attributed to the large shunt resistance typical of WO$_3$-based devices. It is believed that the considerable $R_{SH}$ leads to lower charge carrier recombination and
ultimately results in higher FFs and open circuit voltage. Figure 10

Figure 10

shows a conventional solar cell with the WO$_3$ metal oxide structure sandwiched between the P3HT:PC$_{60}$BM and ITO layers. This structure improves OSC performance via a number of mechanisms including minimizing charge carrier recombination, preventing excitons from coming into contact with the electrodes, and “tuning” the effective work function of the electrodes. Figure 11 shows J-V characteristics for a device having no active layer (ITO/ WO$_3$ (70 nm)/Al) (a) and for one having additional layers ITO/x/P3HT/Ca/Al [x=WO$_3$ (black) or PEDOT:PSS (orange)] under illumination (solid line) and under dark conditions (dashed line) (b). For the device with no active layer, the J-V curve is linear across the entire voltage range. Much like a typical resistor, the slope of this curve can be used to calculate the resistance (or conductivity) of the device. In this particular case, the conductivity was calculated to be (6 +/- 1)e-6 S/cm$^2$. This conductivity is acceptable in an OSC and would indicate that only an excessively thick oxide layer would contribute negatively to series resistance. The work function of the anode is critical as it directly impacts the value of $V_{oc}$. Since the work functions of PEDOT:PSS and WO$_3$ are comparable at (5.1-5.2 eV) to (4.7-6.4 eV), respectively, the oxide would serve as a suitable replacement for PEDOT:PSS without the attendant problems mentioned previously. Fig. 12 shows a graph of the current density vs. voltage characteristics for a series of devices with, and without, buffer layers included. Illumination was simulated AM1.5G at an intensity of 100 mW/cm$^2$. The active layers were fabricated using P3HT:PC$_{60}$BM. The inset shows the semi-logarithmic J-V plot of the cell with a 30 nm-thick WO$_3$ film (which was fabricated separately) for both dark (solid) and illumination (short dash) cases. The device that showed the highest Jsc, FF, and efficiency used a 5 nm-thick oxide buffer layer. Values were 7.6 mA/cm$^2$, 0.69, and 3.1%, respectively. It should be noted, however, that WO$_3$ oxide layer thickness does not markedly impact device performance. Even the device fabricated with a 30 nm-thick layer showed a PCE of 3.1% and FF of 0.70. Still,
these results are considerably better than those for PEDOT:PSS-, or ITO-based cells. In addition, WO$_3$-based solar cells have high shunt resistances and Voc values that are equal to, or higher than, PEDOT:PSS- and ITO-based devices\textsuperscript{27}.

**Molybdenum Oxide (MoO$_3$)**

Using a conventional OSC configuration, MoO$_3$ buffer layers can be used to passivate the ITO anode to improve device performance. Shrotriya, et al., used an oxide layer between an ITO anode and P3HT:PC$_{60}$BM active layer to achieve efficiencies up to 3.3% under AM1.5G simulated illumination\textsuperscript{24}. For purposes of comparison, the researchers simultaneously constructed and tested cells incorporating vanadium oxide (V$_2$O$_5$) buffer layers. Cells were constructed by thermally evaporating the metal oxides (MoO$_3$ and V$_2$O$_5$) or spin-coating PEDOT:PSS. These materials serve as hole injection layers that facilitate charge transport to the ITO layer. The cathode, an electron collector, was made of Ca and, by necessity, a low work function metal (Al). Including the oxide layers is known to increase both Voc and FF in OSCs though the extent to which this occurs is strongly dependent on the oxide thickness. In this study, the V$_2$O$_5$ was $\sim$3 nm while the MoO$_3$ layer measured $\sim$5 nm. The energy band diagram for the constituent materials used in the devices is shown in Figure 13.

By comparison, MoO$_3$ showed higher energy conversion efficiency than both V$_2$O$_5$ and PEDOT:PSS. J-V characteristics can be seen in Figure 14 where data for PEDOT:PSS are also included.

The figure shows similar J-V data for all three buffer layers which indicates that the metal oxides could be suitable substitutes for PEDOT:PSS. Note that Voc is the same for all three materials despite the fact each has a different work function (V$_2$O$_5$ = 4.7eV, MoO$_3$ = 5.3eV, and PEDOT = 5.2eV). There is some debate in the literature as to why the Voc is independent of anode work function, but possible explanations are that the Fermi-level of the oxide work function is pinned to the HOMO of the donor (P3HT) or that the VOC is primarily determined by the relative energy levels of the donor and acceptor\textsuperscript{24}. A parameter that will impact the FF is the thickness of the buffer layer. Increased thickness will raise the series resistance and lower current. This subsequently lowers the fill factor. Still, it’s critical to optimize the thickness in order to simultaneously minimize R$_s$ and provide a homogeneous contact between the ITO and active layer that will eliminate or reduce leakage current. The affects of different oxide layer thicknesses can be seen in the J-V characteristic curves in Figure 15.
Conclusion

Metal oxide semiconductors are showing promise as charge carrier buffer layers and optical spacers in OSCs. These materials show a number of characteristics that make them more attractive than PEDOT:PSS including physical and chemical stability, resistance to thermal degradation, good transport capability, non-toxicity, and ease of processing. Thermal annealing is not necessary during the fabrication process and many of the oxides can be solution-processed. Additionally, metal oxides can serve as protective barriers for the electrodes that increase shunt resistance and prevent leakage current. While there are still obstacles to facile fabrication of the more complicated nanostructured OSC devices, oxides will likely become a very commonly used material for organic solar cell fabrication in the future.

Acknowledgments

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REFERENCES


A significant observation is that the curves for 1 nm thicknesses actually represent two overlapping J-V curves. There is an overlap between the oxide-, and ITO-only contributions. This is due to insufficient oxide coverage on the ITO where the MoO₃ and V₂O₅ form a discontinuous film on the anode. The decrease in FF is significant and most pronounced in the MoO₃ device. A tabular representation of the characterization parameters obtained for the devices based on choice of buffer layer and thicknesses is shown in Table 1 below.

Table 1

<table>
<thead>
<tr>
<th>Anode</th>
<th>JSC (mA/cm²)</th>
<th>VOC (V)</th>
<th>FF</th>
<th>PCT (%)</th>
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<tbody>
<tr>
<td>ITO</td>
<td>7.82</td>
<td>0.40</td>
<td>51.1</td>
<td>1.96</td>
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<td>ITO/3%MoO₃/PSS (25 mm)</td>
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<td>59.6</td>
<td>3.18</td>
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<td>ITO/V₂O₅ (1 mm)</td>
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<td>0.59</td>
<td>47.5</td>
<td>2.48</td>
</tr>
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<td>ITO/V₂O₅ (5 mm)</td>
<td>6.83</td>
<td>0.59</td>
<td>59.3</td>
<td>3.10</td>
</tr>
<tr>
<td>ITO/V₂O₅ (10 mm)</td>
<td>7.16</td>
<td>0.59</td>
<td>57.2</td>
<td>2.08</td>
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<tr>
<td>ITO/MoO₃ (1 mm)</td>
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<td>0.59</td>
<td>42.3</td>
<td>1.98</td>
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<tr>
<td>ITO/MoO₃ (5 mm)</td>
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<td>0.59</td>
<td>58.3</td>
<td>3.06</td>
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<tr>
<td>ITO/MoO₃ (10 mm)</td>
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<td>0.60</td>
<td>61.9</td>
<td>3.33</td>
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<tr>
<td>ITO/MoO₃ (20 mm)</td>
<td>7.73</td>
<td>0.60</td>
<td>59.8</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Table 1


