Organic-Based Solar Cells

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Currently the world consumes an average of 13 TW of power. By the year 2050, this amount will likely grow to 30 TW as the world's population increases and the standard of living in developing countries improves. If this power is provided by burning fossil fuels, the concentration of carbon dioxide in the atmosphere will more than double and substantial global warming, along with many undesirable consequences, will likely occur. Therefore, one of the greatest and most important challenges that engineers face is finding a way to provide the world with 30 TW of power without releasing carbon into the atmosphere. While it is possible that this may be done by using carbon sequestration along with fossil fuels or by greatly expanding our use of nuclear power plants, it is clearly desirable to develop renewable sources of energy. The sun deposits 120,000 TW of radiation on the surface of the earth, so there is clearly enough power available if an efficient means of harvesting solar energy can be developed.

Today, only a very small fraction of our power in generated by solar cells, which convert solar energy into electricity, because they are too expensive.(Lewis and Crabtree 2005) More than 95 % of the solar cells in use are made of crystalline silicon. The efficiency of the most common panels is approximately 10 %, while the cost is \$350/m^2. Put another way, the cost of the panels is \$3.50 per Watt of electricity produced in peak sunlight. When the cost of installation, panel support, wiring and DC to AC converters is included, the price is approximately \$6/W. Over the lifetime of the panels, which is approximately 30 years, the average cost of the electricity generated is \$0.3/kW-hr. In most parts of the United States, electricity costs about \$0.06/KW-hr. We can therefore see that it costs approximately five times more to get electricity from solar cells. Thus, if the cost of producing solar cells could reduced by a factor of ten, it would not only be environmentally favorable to use solar cells, but it would also be economically favorable.

Although crystalline silicon solar cells will get cheaper as economies of scale are realized, it is clear that dicing and polishing wafers will always be somewhat expensive and that it is desirable to find a cheaper way to make the cells. The ultimate method of manufacturing would be depositing electrodes and semiconductors on rolls of plastic or metal in roll-to-roll coating machines, similar to those used to make photographic film or newspapers. Solar cells made this way would not only be cheaper, but could also be directly incorporated into roofing materials to reduce installation costs. Organic semiconductors can be dissolved in common solvents and sprayed or printed onto substrates, so they are very promising candidates for this application.

The first organic solar cells were made by sandwiching thin films of organic semiconductors between two electrodes with different work functions. The work function is the amount of energy needed to pull an electron from a material. When such a diode is made, electrons from the low work function metal flow to the high work function metal until the Fermi levels are equalized throughout the structure. This sets up a built-in electric field in the semiconductor. When the organic semiconductor absorbs light, electrons are created in the conduction band and holes (positive charge carriers) are created in the valence band. In principle, the built-in electric field can pull the photogenerated electrons to the low-work function electrode and holes to the high-work function electrode, thereby generating a current and voltage (Fig. 1a). In practice, however, these cells have very low energy conversion efficiency (< 0.1 %) because the electrons and holes form bound electron-hole pairs called excitons that are not effectively split by the electric field.(Gregg 2003) Most of the time the electrons and holes recombine to give off light by a process known as geminate recombination.

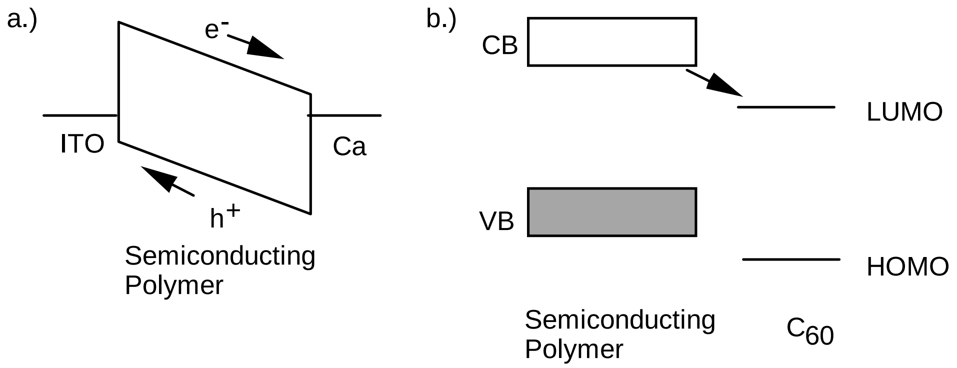
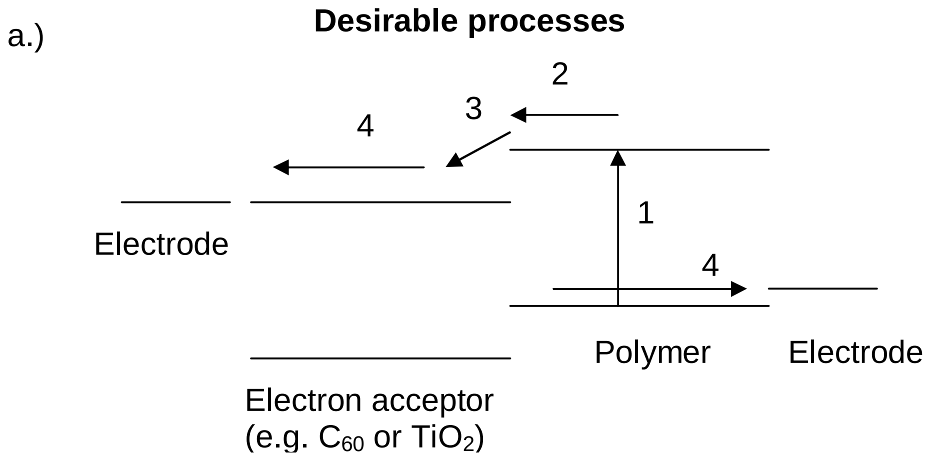


Figure 1: a.) A schematic diagram of the energy bands in a semiconductor polymer solar cell. Indium-tin oxide (ITO) serves as a transparent high work function electrode. Ca serves as the low work function electrode. b.) The schematic energy band diagram for photoinduced electron transfer from the conduction band (CB) of a semiconducting polymer to the lowest unoccupied molecular orbital (LUMO) of C_{60}.

In the mid 1990's it was shown that excitons can be split by electron transfer before the electron and hole recombine if C_{60} derivatives are blended into the polymer. The transfer occurs since these derivatives have an empty energy level that is lower in energy than the conduction band of the polymer (Fig. 1b).(Yu, Gao et al. 1995) It was found that excitons could travel over a distance of approximately 5-10 nm to reach an electron accepting molecule. Solar cells were made simply by blending the C_{60} derivative into the polymer at concentrations in the range of 18-80 wt. %. At these concentrations, the polymer and the C_{60} derivatives form a connected network to each electrode. Consequently, holes can be carried by the polymer to one electrode and electrons can be carried in the C_{60} derivative to the other electrode. Currently, the best solar cells made by this method have an energy conversion efficiency of 3.5 % under solar AM 1.5 conditions.(Shaheen, Brabec et al. 2001; Padinger, Rittberger et al. 2003) Similar devices made with electron acceptors such as CdSe nanorods,(Huynh, Dittmer et al. 2002) a second polymer,(Granström, Petritsch et al. 1998) or titania nanocrystals(Arango, Carter et al. 1999) instead of the C_{60} derivative have a similar, but slightly lower efficiency. Solar cells containing interpenetrating networks of semiconductors with offset energy levels are known as bulk heterojunction devices.

To understand what limits the performance of bulk heterojunction devices and make plans for improving them, it is important to consider all of the processes that must occur inside the cells for electricity to be generated. These processes, shown below, are light absorption (1), exciton transport to the interface between the two semiconductors (2), forward electron transfer (3) and charge transport (4). One must also consider undesirable recombination processes that can limit the performance of the cell, such as geminate recombination of electrons and holes in the polymer (5) and back electron transfer from the electron acceptor to the polymer (6).



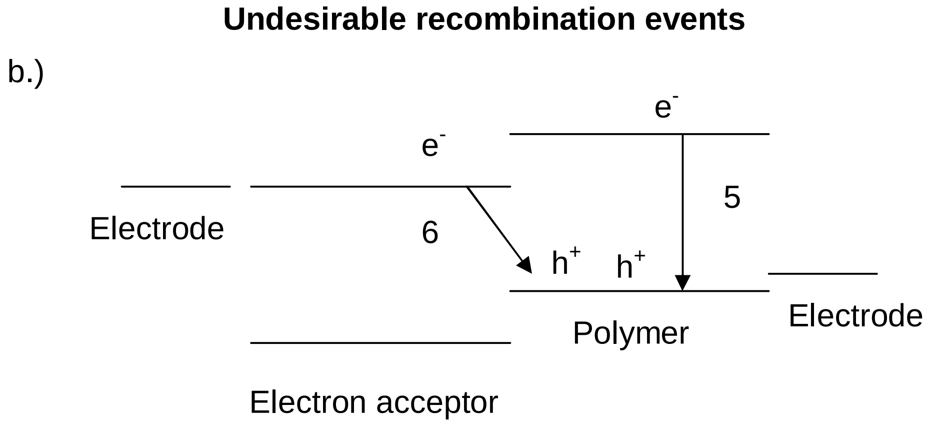


Figure 2 : A schematic energy diagram of the semiconductors and energy levels in a bulk heterojunction solar cell showing the desirable and undesirable processes that can occur. These processes are labeled in the main text.

Consideration of the need to absorb most of the solar spectrum sets two requirements. The first is that the band gap should be small enough to enable the polymer to absorb most of the light in the solar spectrum. Calculations to determine the band gap that optimizes the amount of the light that can be absorbed and the voltage that can be generated show that the ideal band gap is approximately 1.5 eV.(Coakley and McGehee 2004) The second requirement is that the film should be thick enough to absorb most of the light. For most organic semiconductors, this means that the films need to be 150-300 nm thick, depending on how much of the films consists of a non-absorbing electron acceptor.

Once an exciton is created in the polymer, it must diffuse or travel by resonance energy transfer to the interface with the other semiconductor and be split by electron transfer before it recombines. Experiments have shown that an exciton can diffuse approximately 5 nm in most semiconducting polymers before recombination. It is therefore, important to make sure that there are no regions in the polymer that are farther than 5 nm from an interface. There are some small molecule semiconductors with larger exciton diffusion lengths.(Peumans, Yakimov et al. 2003) Research is under way to improve exciton transport in organic semiconductors.

After forward electron transfer, the holes in the polymer and the electrons in the electron acceptor must reach the electrodes before the electrons in the acceptor undergo back electron transfer to the polymer. In the best bulk heterojunction cells, this competition limits the efficiency of the cells. The problem is usually avoided to some extent by making cells that are only 100-nm thick so that the carriers do not have to travel very far. Unfortunately, most of the light is not absorbed by films this thin. If the films are made thick enough to absorb most of the light, then only a small fraction of the carriers escape the device. Many researchers are now striving to optimize the interface between the two semiconductors and improve charge transport in the films so that the charge can be extracted from 300-nm-thick films before recombination occurs.

The outlook for organic solar cells is very bright. Efficiency greater than 5 % has been achieved(Xue, Uchida et al. 2004) and many are optimistic that 20 % can be achieved by optimizing the processes described above. Once this goal is achieved, a primary research challenge will be making cells that are stable in sunlight and that can handle the wide temperature swings that solar cells must endure. The facts that many organic pigments in car paints are able to survive in sunlight and that organic light-emitting diodes with operational lifetimes greater than 50,000 hours are being made provide good hope that the required stability can be achieved. The final challenge will be scaling up the process and manufacturing the cells at a cost of approximately \$30/m^2. Several approaches to making organic solar cells are reviewed in more detail in the January 2005 issue of the Materials Research Society Bulletin.

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