

ET3034TUx - 5.5 - Organic PV Technology

In this block we leave solar cell technology based on inorganic semiconductor materials like amorphous and nanocrystalline silicon, CdTe, CIGS and III-V semiconductor materials.

We are going to look at organic solar cells, like polymer cells or dye-sensitized solar cells.

The materials used are conductive organic polymers or organic molecules.

All these materials can be considered as large conjugated systems.

The organic polymers and molecules consist of large compounds based on carbon.

The carbon may form cyclic or a-cyclic, linear or mixed compound structures.

Here we have some example of organic materials used for PV applications: P3HT, phtalocyanine, PCBM and ruthenium dye N3.

The conjugated system means that carbon atoms in the chain has an alternating single or a double bond and every atom in the chain has a p-orbital available.

The classical example from chemistry classes is the benzene molecule which is a cyclic conjugated compound.

These p-orbitals in the conjugated orbitals are delocalized.

This means that they can form one big mixed orbital.

The valence electron of the original p-orbital is shared over all the orbitals.

Here you see the example of the benzene ring.

This molecule has 6 carbon atoms and six p-orbitals.

They mix forming two circle orbitals that are occupied by a total of 6 electrons.

These electrons do not belong to one single atom, but to a group of atoms.

A methane molecule, which is tetrahedrally coordinated has 4 equivalent sp^3 hydride bonds, with a bond angle of 109 degrees as we discussed in week 2.

Here we see an ethene molecule, which has 3 equivalent sp^2 hybrid bonds with a bond angle of 120 degrees, plus an electron in a p-z orbital.

Two neighboring p-z orbitals form a so-called pi-orbital.

In week 2 we have discussed that two individual sp^3 hybrid orbitals of a Si atom, can make an anti-bonding and bonding state.

The same is valid for the two p-z orbitals making a molecular pi-orbital.

They make a bond and anti-bonding pi-state.

Therefore, conjugated molecules can have similar properties as semiconductor materials.

Most electrons are at room temperature in the bonding state, also referred to as the highest occupied molecular orbital (HOMO).

The anti-bonding state can be considered as the lowest unoccupied molecular orbital (LUMO).

As the conjugated molecules are getting longer, the HOMO and LUMO will broaden and act like a kind of valence and conduction band.

The energy difference between the HOMO and the LUMO can be considered as the band gap of the polymer material.

To discuss whether an organic material is p-type or n-type we have to discuss one concept, which I did not discuss so far: the vacuum level.

The vacuum level refers to the energy of a free stationary electron that is outside of any material, or in other words in a vacuum.

This level is often used as the level of alignment for the energy levels of two different materials.

The ionization energy is the energy needed to excite an electron from the valence band or HOMO to the vacuum state.

The electron affinity is the energy obtained by moving an electron from the vacuum just outside the semiconductor or conjugated polymer to the bottom of the conduction band or LUMO.

It means when a molecular material has a low ionization potential, it can with a relatively ease release an electron out of the material, i.e.

it can act as an electron donor.

When a molecular material has a high electron affinity, it can easily accept an additional electron in the LUMO or conduction band.

Another important aspect of exciting charge carriers in organic materials is that it differs from that of inorganic semiconductor materials discussed so far.

In inorganic semiconductors we can excite an electron from the valence band and conduction band, leaving a hole in the valence band.

In a semiconductor such hole-pair is weakly bound and both entities are easily separated and can diffuse away from each other.

In organic materials this is not the case.

Light excitation results in so-called excitons, which are excited electron and hole pairs, which are still in bound state, due to the mutual coulombic force between the particles.

The exciton can diffuse through the material.

These excitons have a low lifetime in organic materials, they recombine back to the ground state within a few nanoseconds meaning that the diffusion length of such excitons is in the order of only 10 nm.

Let's make a solar cell out of the conjugated materials.

Here we consider an organic PV device, based on an electron donor type and an electron acceptor type material.

Similar like for semiconductor materials, a heterojunction based on two intrinsic materials can be constructed.

The junction is based on two different semiconductor materials or different conjugated compounds.

Here we line up the electron donor conjugated polymer and an electron acceptor conjugated polymer.

The HOMO and LUMO of both polymers can be aligned considering their energy levels with reference to the vacuum level.

At the interface between both layers we see a difference in the HOMO and LUMO levels.

This difference between the HOMO and LUMO represents an electrostatic force between the two layers.

The material can be chosen properly to make the difference large enough, so these local electric fields are strong, which may break up the excitons.

An electron is injected in the electron acceptor and a hole remains in the electron donor material.

A problem of this device concept is that the diffusion length of the exciton is only 10 nm.

It means that in this simple configuration the thickness of the solar cell is limited by the diffusion length, while the thickness has to be at least 100 nm to absorb enough light.

Therefore, the organic solar cells are based on bulk heterojunction photovoltaic devices.

In such device the electron-donor and the electron-acceptor materials are mixed together.

Typical length scales of the mixture of the blend equal to the exciton diffusion lengths can be achieved.

As a result a large fraction of the excitons excited in the material due to light absorption can reach an interface, where they are separated into an electron and a hole.

The electrons move through the acceptor material to the electrode.

The holes move through the donor material to be collected at the other electrode.

The holes are usually collected at a TCO electrode like ITO.

The electrons are collected at a metal back electrode.

The record organic solar cells are based on double junctions nowadays.

Heliatek achieved a 12.0% solar cell efficiency on lab-scale.

The stability of these cells is unknown.

An advantage of organic solar cells is that they have a low production cost.

Chemical engineering allows a large flexibility in band gap engineering.

The organic solar cells can be integrated into flexible substrates.

Important disadvantages are a low efficiency, low stability and low strength compared to inorganic PV cells.

Although organic solar cells can be cheaply, the need of highly expensive encapsulation materials to stabilize the organic PV products limits the industrial application.

To my knowledge, no company is producing organic solar cells at the moment.

Konarka Technologies has been active in the past.

The small solar modules had efficiencies in the range of 3 up to 5% and lasted only a couple of years.

An alternative solar cell concept based on organic materials is the so-called dye-sensitized solar cell.

It is a photoelectrochemical system.

It contains TiO₂ nanoparticles, dye-particles, an electrolyte and a platinum contact.

In this illustration the dye-sensitized solar cell is schematically shown.

Let's consider first the photoactive parts of the solar cell which consists of the photoactive dye-sensitizer which acts like an electron donor.

The second material is TiO₂ nanoparticles which acts like the electron acceptor.

The dye-material is mixed with TiO₂ material like organic bulk heterojunction solar cells.

The photoactive material is the so-called dye-photosensitizer: ruthenium polypyridine.

If a photon is absorbed by the ruthenium polypyridine, it can excite an electron from its ground state, referred to as S, to an excited state, referred to as S*.

In this case the S can be considered as the HOMO and the S* state can be consider as the LUMO.

The S* state lies higher in energy than the energy level of the conduction band of the TiO₂.

As a result the light-excited electrons are injected into the TiO₂ nanoparticles.

The photosensitizer molecule remains like a positively charged entity.

The electrons in the TiO₂ move to the TCO-based back contact.

The transport mechanism is diffusion based.

The electrons diffuse between the various TiO₂ nanoparticles until they arrive at the TCO contact.

Through the electric circuit the electrons move to the counter electrode, in other words the other contact.

Between the counter electrode and the dye, a so-called electrolyte is placed.

Electrolytes are solutions or compounds that contain ionized entities that can conduct electricity.

Typical electrolyte contains iodine.

The positively charged oxidized dye molecule is neutralized by a negatively charged iodide.

Three negatively charged iodides neutralize two dye molecules and create one negatively charged triiodide.

This negatively charged triiodide moves to the counter electrode where it is reduced using two electrons into three negatively charged iodines.

These photoelectrochemical cells require a platinum back contact to facilitate the reactions.

As a result the performance of a dye-sensitized solar cell depends on the HOMO and LUMO level of the dye material, the Fermi level of the TiO₂ nanoparticles and the so-called redox potential of the iodide and triiodide reactions.

The record efficiency of dye-sensitized PV device on lab-scale is currently 14.1% as achieved at EPFL in Switzerland.

The advantage of dye-sensitized PV devices are the low cost price of producing the device.

A disadvantage is the stability of the electrolyte under various weather conditions.

At lower temperature the electrolyte can freeze.

This stops the power production and it might result in physical damage.

Higher temperatures result in significant expansion of the electrolyte, which make encapsulation of modules more complicated.

The dye-sensitized PV technology is facing some more challenges, one is replacing the expensive platinum electrode material with other cheaper materials.

The second one is the development of more stable and resistive electrolyte materials.

The third one is the development of improved dyes, improving the spectral and band gap utilization of the solar cells.

A dye-sensitized PV product is not yet available on the commercial market.

In this week I have introduced you to various PV technologies.

Next week, we will shortly discuss the so-called third generation PV concepts.

In addition, we will look at alternative solar technologies, which not only produce electricity, but heat or solar fuels as well.

See you next week!