Organic photovoltaic cells: towards an all-polymer path...

Beyond improved performance for photovoltaic devices, in terms of efficiency and reliability, the real challenge is to achieve significant cost reductions per kilowatt-hour generated. Plastic or polymer organic materials, affording great ease of utilization, are on course to gain acceptance, alongside silicon, for solar cell fabrication, even though technological barriers do still remain, that need to be overcome.

While the **photovoltaic cell** market is currently dominated, to over 90%, by **crystalline silicon**, organic-inorganic **composites**, still at the stage of market-introduction feasibility studies, in terms of efficiency and reliability, are on their way to gaining acceptance in those areas where silicon technologies, and more broadly inorganic technologies, can claim no favorable position, or are not on course to gain one. The organic path, i.e. use of plastics, these being less expensive, is indeed increasingly seen as a complementary path for the future that is both attractive and credible. Being degradable, **polymers** can guarantee a clean technology, in a sustainable development context. Owing to their ease of handling, selecting them as base material would allow manufacturers to implement, for the entirety of cell engineering (from substrate to protective casing), but one and the same inexpensive technology, this being close to proven printing processes (pass-by processes). As a further benefit, such plastics would also allow expanding the offer from manufacturers, to include flexible products, or in a variety of shapes and configurations (construction tiles, for instance), opening up markets not accessible to conventional technologies, in particular through integration into multifunctional systems.


F. Vigouroux/CEA

Plastic photovoltaic cell fabrication and characterization platform at GENEC.

Operating principle of an organic photovoltaic cell

Following absorption of **photons** by the **polymer**, bound **electron-hole pairs** (excitons) are generated, subsequently undergoing dissociation. Owing to inherent limitations in organic materials (exciton lifetime, low charge mobility), only a small fraction of photon-generated electron-hole pairs effectively contribute to the photocurrent. One of the main ideas is to achieve volume distribution of the photogeneration sites, to enhance exciton dissociation. This approach is based on increasing **junction** surface area, through deployment of an interpenetrating network of the donor-acceptor (D-A) type, effecting transport of holes (P^+) to the **anode** (indium-tin oxide [ITO]), and of electrons (e^-) to the metallic **cathode** (made e.g. of aluminum [Al]). While quantum separation efficiency, for photoinduced charges in systems associating a **semiconducting** polymer (of PPV or polythiophene type) with a fullerene derivative (PCBM), is thus close to unity, the challenge now is to restrict recombination and trapping processes limiting charge transport and collection at the electrodes, to improve overall device efficiency, this currently still being low (less than 5%). The rise of the pathway is also heavily dependent on mastery and understanding of cell aging mechanisms, but equally on mastery of thin-film technologies, to achieve protection of the device against atmospheric oxygen and water vapor.

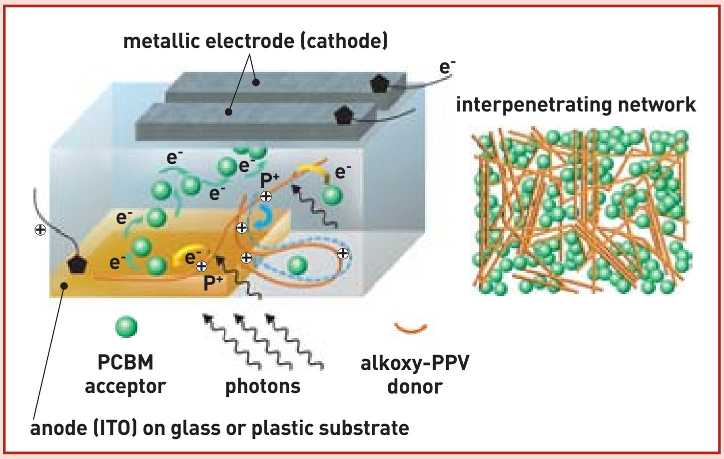


Figure from a presentation by S. Sariciftci (www.lios.at)

The blue dotted line shows the trajectory of holes inside the material.

A new takeoff

Use of organic materials for photovoltaic applications has been the subject of intensive investigation for the past twenty years (see Box). Failing an innovative approach, these initial investigations were stymied by low **conversion efficiencies** for these materials. Research has picked up again quite strongly over the past six or seven years, in Europe, the United States and Japan, witnessing a drive impelled, on the one hand, by recent advances made, in particular, in the area of electroluminescent displays, and, on the other, by discovery of innovative materials, and the bringing into use of novel types of **junction**.

Current developments should make it possible to look to initial commercial products in 2005 (this timeframe being recently mentioned by Siemens), and, in the longer term, to achieve competitive production costs. For the time being, numerous technological barriers still have to be overcome, in particular as regards materials, component architecture, and fabrication techniques.

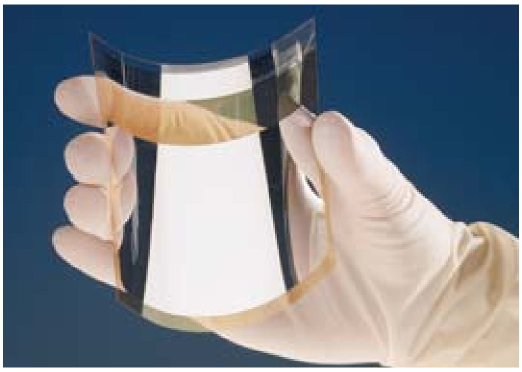
A nationwide network of collaborations

Initiated as early as 1996 in the context of a PhD research project, and under the aegis of a European contract, work on this topic at CEA's Innovation Laboratory for New Energy Technologies and Nanomaterials (LITEN: Laboratoire d'innovations pour les technologies des énergies nouvelles et les nanomatériaux) has resulted, in particular, in a patent relating to an original physical principle, this allowing, through induction of an internal electric field set up by the orientation of **polar** molecules in the structure, significant increases in charge collection.

Since early 2003, the Cell and Components Laboratory in CEA's Photovoltaics and Electrochemical Storage Service (GENEC) has been piloting a French nationwide project, bringing together teams working on upstream research at CEA, **CNRS**, and in academe (CSPVP Program: Cellules solaires photovoltaiques plastiques - Plastic Photovoltaic Solar Cells). The aim? To leverage the synergy from complementary teams, to cross swiftly a credibility threshold within the international community, and play a central, strategic part in the setting up of an industrial pathway.

Bringing down the cost per kilowatt-hour: an ambitious program

Less than one euro per **watt**, with plastic cells: such is the target set for the CSPVP Program. This ambitious program, at an overall cost of 10 million euros, jointly funded by **Ademe**, has taken up the challenge of demonstrating, inside four years, the advantage of this pathway, and, initially, the feasibility of polymer photovoltaic cells exhibiting efficiency higher than 5% under solar illumination, and good stability over 5,000 hours at least. For that purpose, the teams, presently based at the Saclay Center, can avail themselves of a large (100-mm × 100-mm) prototype cell fabrication line, in glovebox conditions, along with plentiful **nanostructuration** and optoelectronic characterization resources. Investigations by means of surface analysis methods, in particular, were initiated in collaboration with other CEA components - the National Nuclear Science and Technology Institute (INSTN: Institut national des sciences et techniques nucléaires), the Solid State, Atoms and Molecules Research Department (DRECAM: Département de recherche sur l'état condensé, les atomes et les molécules), and the Pierre-Süe Laboratory (LPS) - to achieve process optimization, and gain a better understanding of cell aging mechanisms. A test bench, using the time of flight method, has also been set up, to allow systematic measurements of charge mobility in cell active material. Outcomes, after 18 months, are encouraging, since efficiencies are now over the 3% mark, and new, optimized materials have been synthesized.


A. Gonin/CEA

Large (100-mm × 100-mm) flexible plastic solar cell, fabricated at GENEC.


P. Stroppa/CEA

One of the fabrication steps for polymer photovoltaic cells: spin deposition of the photoactive polymer material.

Fruitful international collaborations

In June 2002, a research partnership was signed with Johannes Kepler University, Linz (Austria), leaders in the field, and CEA engineers have already spent some weeks in Austria. A privileged relationship has also been set up with IMEC-IMOMEC, (1) concerning supply of ultrapure materials (**conjugate polymers**).

Under the aegis of the European **6th Framework Program**, finally, CEA/LITEN has taken up an ambitious position, with the coordination, from the beginning of 2004, of a STREP (small targeted research project) effort, the Molecular Orientation, Low Bandgap and New Hybrid Device Concepts for the Improvement of Flexible Organic Solar Cells (MOLYCELL) Program. This structuring network brings together, around two manufacturers, Siemens and Konarka, nine major research laboratories, recognized in the field of organic materials and technologies, including IMEC, the Linz Institute for Organic Solar Cells, the Federal Institute of Technology (École polytechnique fédérale), Lausanne (Switzerland), the Fraunhofer Institute for Solar Energy Systems (Germany), the Energy Research Center of the Netherlands, and Imperial College, London (United Kingdom).

This ambitious program, with an overall budget of €4.5 M over 30 months, is taking up the challenge of overcoming the major remaining barriers, to enable the rise of competitive fabrication pathways for all-organic and hybrid photovoltaic cells.

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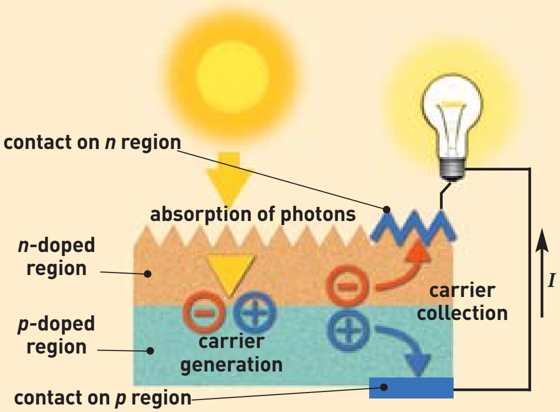
(1) IMEC-IMOMEC: IMOMEC (Institute for Materials Research in Microelectronics) is a division of IMEC (Interuniversity Microelectronics Center), an independent European research center, based in Belgium.

D How does a photovoltaic solar cell work?



The photovoltaic effect used in solar cells allows direct conversion of light energy from the Sun's rays into electricity, by way of the generation, and transport inside a semiconductor material, of positive and negative electric charges, through the action of light. This material features two regions, one exhibiting an excess of electrons, the other an electron deficit, respectively referred to as *n-type doped*, and *p-type doped*. When the former is brought into contact with the latter, excess electrons from the *n* material diffuse into the *p* material. The initially *n*-doped region becomes positively charged, and the initially *p*-doped region negatively charged. An electric field is thus set up between them, tending to force electrons back into the *n* region, and holes back into the *p* region. A junction (so-called *p-n* junction) has been set up. By placing metallic contacts on the *n* and *p* regions, a diode is obtained. When the junction is illuminated, photons having an energy equal to, or higher than, the width of the forbidden band, or band gap, yield their energy to the atoms, each photon causing an electron to move from the valence band to the conduction band, leaving behind it in turn a hole, also able to move around the material, thus giving rise to an electron-hole pair. Should a load be positioned at the cell's terminals, electrons from the *n* region will migrate back to the holes in the *p* region, by way of the outside connection, giving rise to a potential difference: an electric current passes (see Figure).

The effect thus involves, basically, the material's semiconducting properties, and its doping, to improve conductivity. Silicon, now used in most cells, was selected for the presence of four valence electrons in its outermost shell (column IV of the Mendeleyev periodic table). In solid silicon, each atom - termed a tetravalent atom - is bound to four neighbors, and all electrons in the outermost shell participate in the bonds. Should a silicon atom be substituted for by an atom from column V (a phosphorus atom, for instance), one of its five valence electrons is not involved in the bonds; as a result of thermal agitation, it soon moves to the conduction band, thus becoming free to move through the crystal, leaving behind it an immobile hole, bound to the doping atom. There is electron conduction, and the semiconductor is designated as an *n-type doped semiconductor*. If, on the other hand, a silicon atom is substituted for by an atom from column III (boron, for instance), carrying three valence electrons, one electron is missing, if all bonds are to be maintained, and an electron may quickly move in to fill this gap, taking up the vacant orbital, as a result of thermal agitation. A hole thus arises in the valence band, contributing to conduction, and the semiconductor is said to be a *p-type doped semiconductor*. Atoms of elements such as boron or phosphorus are thus doping agents in silicon. Photovoltaic cells are assembled into modules.

Note: In *Organic photovoltaic cells: towards an all-polymer path...*, you will find the operating principle of organic photovoltaic cells (Box, p. 122).

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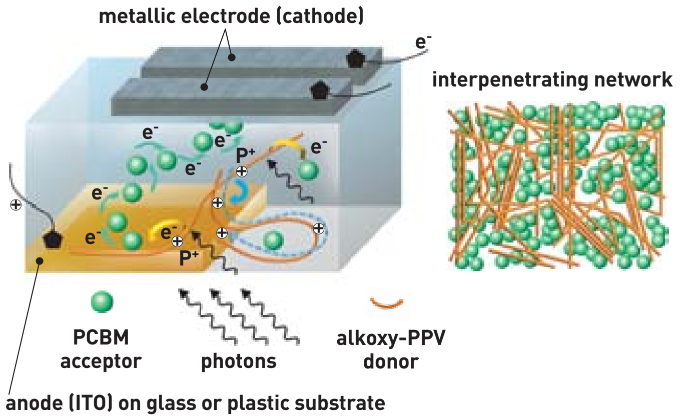

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