Michal Váry, Milan Perný, Martin Kusko, Eduard Firický

ORGANIC SEMICONDUCTORS FOR SOLAR CELLS – AN OVERVIEW

This contribution is focused on organic semiconductors used in photovoltaic, an overview of materials used nowadays for organic solar cells. In particular, we focus on a comparison of important parameters, efficiency and fill factor, for conventional inorganic semiconductor photovoltaic systems and organic PV structure.

Keywords: organic semiconductors, organic materials in photovoltaic, organic solar cells, efficiency, fill factor

I. INTRODUCTION

Huge progress in the field of organic materials is driven by the expectation of new applications with virtually limitless source of those materials that are easily to manufacture, or obtained from nature. During the last twenty years the research in this area has brought great applications such as organic light-emitting devices - OLED, which is already incorporated into commercial products containing OLED displays, logic circuits with organic field effect transistors - OFET, or organic solar photovoltaic cells - OPVC [1]. The following brief overview of PV deals with the properties of organic materials and solar cells made therefrom. Emphasis is placed on the advantages and disadvantages of application of organic materials in this area.

II. MATERIALS AND STRUCTURES FOR SOLAR CELLS

Solar cells are used to convert solar energy into electricity by means of appropriately selected structures. According to the structure of the material used, solar cells are divided into monocrystalline, polycrystalline, multicrystalline and amorphous. According to the construction are divided into single-layer, dual layer and multilayer, according to the origin of the material to organic and inorganic.

Nowadays there are used mixtures of these structures and materials, the so-called heterostructures, where we use a combination of crystalline and amorphous silicon (a-Si/c-Si heterostructures) or inorganic - organic heterostructures, which have potential for high efficiency and other beneficial properties [2]. Tandem solar cells using a layering of semiconducting materials with different band gap widths deposited on the basis of absorption law, thus greatly increasing their effectiveness. Thin layer, in turn, represent a thin semiconductor layer deposition (μm) on the carrier material, while achieving a high savings of semiconductor material [3].

The newest alternative, however, are semiconductors based on organic materials - polymers, oligomers, dendrimers, pigments, dyes and others. Conditions for photovoltaic applications meet the agents and polymers, such as: chlorophyll, anthracene, tetrafenylopyrin, perylene pigment, C60, PPV, and many others [4]. This creates applications like silicon heterostructures, which use inorganic materials together with organic. Production of cells based on organic materials expect in the future available, inexpensive and environmentally demanding applications especially with high efficiency, flexibility, which is very advantageous in the manufacturing process and installations [5,6].

III. ORGANIC SEMICONDUCTORS

The way of charge carriers formation in organic semiconductors is different than in inorganic semiconductor materials. In the organic semiconductor molecules, there is a existence of chemical bonds which after delivery of excitation energy cause change in the state of the molecule. In organic semiconductors is a double bond. These types of bonds occur by overlapping of valence orbitals in the molecule. Resulting bond strength depends on the overlapping. For larger orbital overlap, in the area between the atomic nucleus, is greater probability of an electron occurrence and bond strength is therefore increased. In contrast, if there is no orbital overlapping, no binding arise.

For the effective overlapping is necessary that both the valence orbitals have the same symmetry of the center of the molecule and do not differ too much in the value of excitation energy. Effective atomic orbitals overlapping also cause different types of bonds, known as σ and π bonds. In most cases there is σ bond, by primary interaction of two atoms and it is the most important and most common type of chemical bonding in organic semiconductors. Almost all organic materials are insulators. But when their molecules have π (or σ) associated systems, electrons can move through the overlapping [7].

We define two main groups of organic semiconductors:

- low-molecular lightweight materials that represent the pigments and dyes (anthracene, pentane, TPP - tetrafenyl porphyrins, Alq_3 - 8-hydroxyquinoline aluminum, chlorophyll, perylene pigment, C_{60} - fuleren and others)
- polymers (PFO - polyflorin, PPV - polyphenylene vinyl, MEH-PPV - polymetoxy ethyl-hexyloxy phenylene vinyl and others)

Both groups of materials have a common conjugated, p - electron system from *pz* orbital of the sp^2, hybrid carbon atoms in the molecule. In the molecule is σ-bond arranged and π-bond is significantly weakened. Together, they form a double bond. Therefore, there is a π-π* excitation. Typical width of the energy gap is between 1,5 to 3 eV, which leads to light absorption or emission in the visible light spectrum. Skipping of the charge carriers from molecule on the molecule is dependent on the width of the energy gap between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) [1].

IV. SOLAR CELLS BASED ON ORGANIC SEMICONDUCTORS

Principle of operation of organic solar cells is very similar to that in inorganic semiconductors. Almost all organic solar cells are planar

- layered structures, where the organic light absorption layer is between two electrodes with different work function.

Based on the structures could be organic photovoltaic cells divided into five basic groups:

- single layer cells
- double layer cells or heterojunction solar cells
- blend or bulk heterojunction cells
- laminated cells
- dye-sensitized solar cell

Single-layer solar cells consist of a single thin layer of organic semiconducting material between two appropriate electrodes. The most efficient organic solar cells are based on the generation of charge between two different organic semiconductors, respectively materials.

Double-layer solar cells consist of two semiconductor (p + and n-) imposed between the electrodes. Photo generation occurs at the interface of two layers, called the organic heterojunction. Separation of charges is provided by electrodes and photocurrent arises by charge transportation between the donor and acceptor molecule. Charges arising at the junction are separated by the electrodes and have little chance of recombination, which is the biggest advantage of dual-layer cells and therefore take much better parameters. These cells are among the most efficient organic solar cells [9].

Blend structures are newer types of photovoltaic structures that do not have an exact analogy with inorganic semiconductors. In principle, it is a single-layer structure, but the active layer of organic material is a mixture of donors and acceptors.

Laminated cells are basically a special type of double-layer cells, but the processing of a given structure is different. Separately is p-layer firstly applied to one electrode and n-layer to second electrode, two independent parts arise, which are then combined in technological process. The advantage is much less diffusion of one material to another material at application of layers, control of the properties of A/D junction by heat, pressure or other processes before, during and after lamination and thereby improvement of the interface properties [9].

Dye solar cells deserve a separate classification, as compared with other conventional types of cells are based on the rapid photochemical cyclic regenerative process. For its work using dye to absorb photons, the ionic liquid electrolyte and an inorganic semiconductor (semiconductor nanoparticles) for transfer of the charge [5].

V. THE CURRENT STATUS OF THE USE OF ORGANIC SUBSTANCES IN PHOTOVOLTAICS

There are several reasons for the use of organic materials in photovoltaic applications, the most significant are:

- ease of layers processing
- thickness of the active layer (ηm) and thus the size of the final device
- easy chemical controllability of material parameters (band gap width, electrical conductivity, etc.)
- wide range of very cheap materials and structures
- ability to be applied at room temperature on the quantity of available substrates (plastics, glass, metal foil) with the inherent flexibility

Because the molecules are larger than atoms (eg. silicon) are flexible and light, it is well to work with them. The chemical industry can produce large quantities of organic semiconductors at the same time, with emphasis on structures that absorb sunlight very efficiently. Consequently may be organic solar cells made several orders of magnitude thinner than conventional silicon solar cell. Because they are thin, lightweight and flexible also, are simply to store in the manufacture or before installation at the customer [12]. Organic materials can actually be applied to the substrate surface by means of methods close to spraying or printing technique, which may avoid as strict hygiene standards in production than in inorganic semiconductors. These methods are readily adaptable to continuous manufacturing processes (printing, scrolling) and promise to dramatically reduce production costs and thus the price of these cells (essentially all organic equipment) [13].

A substantial disadvantage of the use of organic semiconducting materials is currently the low efficiency of converting sunlight into electricity, which applies to all concepts used except dye light sensitive cells. Given the messiness of molecular environment, mobility and life time of these systems is very limited. This course reflects efficiency of organic cells. While weak generation and separation of electrical charges limits the efficiency of organic solar cells, another problem is durability. Organic molecules are unstable and react with other molecules (eg. oxygen and water), which may influence their impact on the composition and deterioration of electrical and optical properties. Most importantly, much more organic molecules degrade under the influence of solar radiation and therefore the life of photovoltaic devices in addition to efficiency is one of the biggest problems to solve [10-12].

Energy conversion efficiency η is defined as the ratio of the maximum power output to power of light source (1). Quantum efficiency QE is defined as the number of electrons generated by the absorbed photon. One can define the internal quantum efficiency IQE and external quantum efficiency EQE. The external quantum efficiency takes into account all the photons that hit the surface of the cell, but the internal excludes the reflected photons. Fill factor FF determines the deviation from the theoretical value of the maximum obtainable power (2) [4].

$$\eta = \frac{P_{max}}{P_{light}} = \frac{I_{sc} U_{oc} FF}{P_{light}} \ (\%) \qquad (1)$$

$$FF = \frac{P_{max}}{U_{oc}.I_{sc}} = \frac{U_{max}.I_{max}}{U_{oc}.I_{sc}} \ (-) \qquad (2)$$

The following tables are an update overview on basic parameters of inorganic and organic solar cells commercially available today, or in research. This is a design by June 2010 from the laboratories or companies who develop these devices, which achieved the best results of measurements under the supervision of a certified testing center. Table 1 is the official overview of the most efficient solar cells. Table 2 is a set of ten solar cells with the best measured values measured outside the official declarations of specialists in this field, indicating the manufacturer [14].

Comparing of available tabulated values can be concluded that while such cells based on GaAs achieve efficiency η = 27,5%, fill factor FF = 84,1%, polymer cells reach the value η = 8,3%, FF = 70,2% and organic tandem cells the value η = 8,3%, FF = 59,5%. From cells based on organic materials have the best perspective at this time dye light-sensitive cells. Today show efficiency comparable to amorphous silicon, or even exceeded. For comparison, cell from amorphous silicon has η = 10.1%, FF = 67%, but light-sensitive dye cell has η = 10,4 %, and FF = 65,2% (Tab. 1).

Table 1: Summary of parameters of solar cells from different manufacturers measured under AM1,5 spectrum (1000W/m^2) at T = 25 ° C [14].

Classification	Efficiency [%]	FF [%]
Silicon		
Si (crystalline)	25,0 ± 0,5	82,8
Si (multi crystalline)	20,4 ± 0,5	80,9
Si (thin film submodule)	16,7 ± 0,4	78,2
III-V cells		
GaAs (thin film)	27,6 ± 0,8	84,1
GaAs (multi crystalline)	18,4 ± 0,5	79,7
InP (crystalline)	22,1 ± 0,7	85,4
Thin film Chalcogenide		
CIGS (cell)	19,6 ± 0,6	79,2
CIGS (submodule)	16,7 ± 0,4	75,1
CdTe (cell)	16,7 ± 0,5	75,5
CdTe (submodule)	12,5 ± 0,4	70,5
Amorphous/nano crystalline Si		
Si (amorphous)	10,1 ± 0,3	67
Si (nanocrystalline)	10,1 ± 0,2	76,6
Photochemical		
Dye sensitized	10,4 ± 0,3	65,2
Dye sensitized (submodule)	9,9 ± 0,4	71,4
Organic		
Organic polymer	8,3 ± 0,3	70,2
Organic (submodule)	3,5 ± 0,3	48,3
Tandem/Multijunction		
GaInP/GaAs/Ge	32,0 ± 1,5	85
GaInP/CIS (thin film)	25,8 ± 1,3	–
aSi/μc-Si (thin film cell)	11,9 ± 0,8	68,5
Organic (2-cell tandem)	8,3 ± 0,3	59,5

Between light sensitive dye cells is achieved the highest overall efficiency of cells by Sharp with η = 11,2%, and FF = 72,2% (Tab. 2), Service life of these dye cells is according to [14] 7 years in Central European conditions.

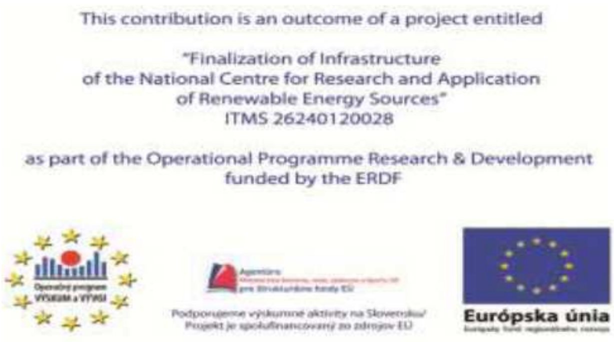
Table 2: Summary of parameters of the ten best solar cells announced by leading experts, measured under AM1,5 spectrum (1000W/m^2) at T = 25 ° C [14].

Classification	Eff. [%]	FF[%]	Description
Silicon			
Si (MCZ crystalline)	24,7 ± 0,5	83,5	UNSW PERL
Si (large crystalline)	24,2 ± 0,7	82,9	Sunpower
Si (large crystalline)	23,0 ± 0,6	80	Sanyo HIT
Si (large multi crystalline)	19,3 ± 0,5	76,4	Mutsubishi El.
Other cells			
GaInP/GaAs//GaInAs	35,8 ± 1,5	85,3	Sharp
CIGS (thin film)	20,3 ± 0,6	77,5	ZSW Stuttgart
a-Si/nc-Si/nc-Si (tandem)	12,5 ± 0,7	68,4	United Solar
Dye-sensitised	11,2 ± 0,3	72,2	Sharp
Luminescent submodule	7,1 ± 0,2	79,5	ECN Petten

VI. CONCLUSION

From the above information may be noted, that semiconductor based low molecular substances and polymers have a long way of research before reaching the desired properties, even though at the market appear first applications of organic solar cells, whilst the greatest success achieved photochemical cells based on organic dyes with a similar effect as that of cells from amorphous silicon. On the other hand perspective, given the existing knowledge achieved after several years of investigation in this area is very promising, especially as regards the simplification of production, price reductions and the possibility of handling a much lighter organic devices.

ACKNOWLEDGMENT



REFERENCES

[1] Brütting, W.: Physic of organic semiconductors. WILEY – VCH Verlag GmbH & Co., Weinheim 2005, ISBN 3-527-40550-X.

[2] Goetzberger, A., et al.: Photovoltaic materials, history, status and outlook. Materials Science and Engineering, 2003 Report vol. 40, 1-46.

[3] Šály, V.: Materiály a materiálové štruktúry pre modernú fotovoltiku. Internet side: <*www.matdesign.sav.sk/data/long_files/saly.pdf*>

[4] Nunzi, J.M.: Organic photovoltaic materials and devices. C. R. Acad. Sci. Paris, 3(4), 523-542 (2002).

[5] Goetzberger, A. et al.: Photovoltaic materials, history, status and outlook. Materials Science and Engineering, 2003 Report vol. 40, 1-46.

[6] Putala, M.: Materiálova chémia. Európsky sociálny fond. Internet side: <*158.195.47.144/clanky/chemia/Materialova_chemia.DOC*>

[7] Internet side: <*http://web.tuke.sk/hfkch/Anorganika/ChemiaI/Kap3Vazba.pdf*>

[8] Sun, S., Sariciftci, N.: Organic photovoltaics: Mechanisms, materials and devices. CRC Press, 2005, ISBN 082475963X, 9780824759636.

[9] Petritsch, K.: Organic Solar Cell Architectures. Cambridge and Graz, July 2000.

[10] Halme, J. : Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests. Internet side: <*www.tkk.fi/Units/AES/studies/dis/halme.pdf*>

[11] Bailey, M., Park, J., Dhirani, A.: Natural Dye-Sensitized Nanocrystalline Solar Cell. Department of Chemistry, University of Toronto. Internet side: <*www.chem.utoronto.ca/staff/DHIRANI/solar%20cell.pdf*>

[12] Kwiatkowski, J . : Organic Photovoltaics: the Good, the Bad, and the Inefficient. 2008, Renewable Energy company article. Internet side: <*www.renewableenergyworld.com/rea/news/article/2008/05/organic-photovoltaics-the-good-the-bad-and-the-inefficient-52410*>

[13] Wadell, A.L., Global Photonic Energy Corp., Dr. Stephen R. Forrest, University of Michigan: High Power Organic Solar Cells from Efficient Utilization of Near-Infrared Solar Energy. 2007, Green Power magazine. Internet side: <*www.aldebaran.cz/bulletin/2007_30/organic-cells.pdf*>

[14] Green, M.A, Emery, K., Hishikawa, Y., Watra, W.: Solar Cell Efficienty Tables (Version 37). 2011, Published online in Wiley InterScience 19:84-92.

ADDRESSES OF AUTHORS

Michal Váry, Milan Perný, Martin Kusko, Eduard Firický, Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Institute of Power and Applied Electrical Engineering, Department of Elektrotechnology, Ilkovičova 3, Bratislava, SK 812 19, Slovak Republic, michal.vary@stuba.sk, milan.perny@stuba.sk, martin.kusko@stuba.sk, xfiricky@stuba.sk