

DYE-SENSITIZED SOLAR CELLS: MATERIALS AND PROCESSES

Michal SOKOLSKÝ, Július CIRÁK

Department of Physics, Faculty of Electrical Engineering and Information Technology,
Slovak University of Technology, 812 19 Bratislava, Slovak Republic,
e-mail: michal.sokolsky@stuba.sk

ABSTRACT

The dye-sensitized solar cell (DSSC) has been proven to have a good chance to become a notable competitor for solar cells based on today technology of *p-n* junction. The principle of operation of DSSC solar cells in comparison with conventional semiconductor solar cells where light absorption and charge carrier transport are done by the semiconductor is different. In DSSC these two tasks are separate. Charge separation is done by photo-induced injection to the conduction band and such created carriers are transported to charge collector. By using dyes which have broad absorption band, the solar cell is capable to harvest large fraction of sunlight. In this paper the basic construction and mode of operation of solar cells based on dyes is described.

Keywords: dye-sensitized solar cell, nanoporous TiO_2 , organic dye

1. INTRODUCTION

As the storage of a fossil supply is decreasing every year the mankind must look for another source of energy. Even the most powerful source we have now will be depleted some day and there is also a problem with the nuclear waste we must consider. One option is to look for that source in renewable energy technologies such as wind or solar power.

The sun is a primary source of energy for most life forms found on the earth. It is clear, abundant and most of all renewable. Fully grasping the power of the sun we can improve our way of life, reduce our dependence on fossil fuels and stimulate economy by bringing new jobs to the industry.

Every year the use of solar energy technologies is increasing in the world. It provides people with the energy to heat the house (solar thermal energy) or change solar energy right to electricity (photovoltaics) and decrease the dependence on the other sources of power.

1.1. Background

The first panchromatic film, able to remit image in black and white, followed the work of Vofel in Berlin, in which he used dyes and silver halide grains [1]. However, clear recognition and verification of operating principle dates to 1960s, when Gerisher and Tributsh researched a ZnO photoelectrode sensitized by organic dyes [2, 3]. But these cells had low harvesting efficiencies and low photon to current conversion, because as a photoelectrode they used single crystals and polycrystalline materials. Only after the introduction of mesoporous materials such as TiO_2 and using synthesized dyes the performance of these cells improved. By using porous TiO_2 electrodes with a roughness factor of ca. 1000 based on a synthesized dye and iodine I^-/I_3^- redox couple in an organic solvent that Gratzel and O'Regan reported a solar cell with efficiency of 7 to 10 % [4]. Ever since this discovery there was a continuous approach to improve performance, efficiency and stability these solar cells.

2. CONSTRUCTION AND MODE OF OPERATION

A typical DSSC design is shown in Fig. 1.

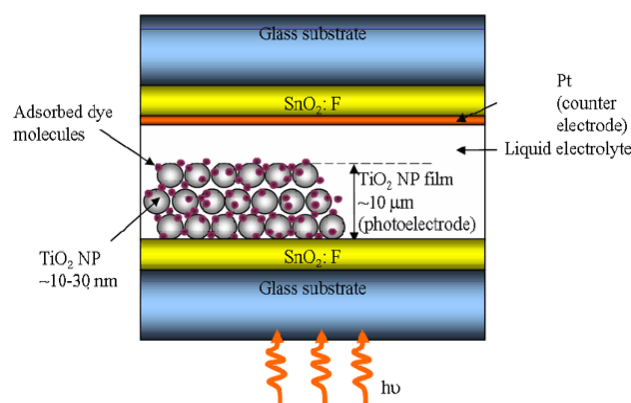


Fig. 1 Typical design of a dye-sensitized solar cell

The support substrate can be glass, although it is possible to use a flexible plastic substrate. The support substrate must be transparent in visible and near UV region because light is coupled into the cell through it. The anode electrode is made of a thin film of a transparent, conducting material, which is deposited on the inner side of the support substrate. For this purpose indium thin oxide (ITO) semiconductor is widely used. Although other semiconductors such as fluorine-doped thin oxide ($\text{SnO}_2:\text{F}$) can be used as well. The real photoanode is formed by a porous film of nanocrystalline semiconductor (TiO_2). These films are usually few micrometers thick (between 1- 10 μm) and can be fabricated in different ways. The most widely used method for fabrication of thin films is casting slurry of the nanocrystals using spray, or drag coating and then calcine the film at 400-450°C. Thus structural stability can be created.

Several methods can be used to produce TiO_2 of varying particle size, from few nanometers to tenths of nanometers and different crystallinity [5]. Wilson et al.

created a microwave method, which produces small crystallites (4-5 nm) with high anathase fraction [6]. An alternative method is to produce highly porous nanostructured titania photoanodes via surfactant templating of titania precursor. These films have completely different morphology from those created slurries of nanocrystals. A relatively new method is to combine those two different methods. First, create small nanocrystals of anathase, and second, to self-assemble these nanocrystals around a suitable template so as to create an ordered mesophase.

Regardless of crystallinity or morphology of the photoanode, the sensitizer is adsorbed on the surface in the form of a monolayer [7]. Many papers have been dedicated to optimise sensitizer [8] in last 15 years, and various sensitizers were observed. But there are three parameters, which the sensitizer assigned to DSSC should possess:

1. Ideally, the sensitizer should be “black” in the UVA, visible, and IR spectral region, with extremely high broadband absorption.
2. The energetic and dynamic coupling between the photo-excited state of the sensitizer and the conduction band of the photoanode: the transfer of an electron between the photo-excited sensitizer and photoanode must be rapid and energetically favourable.
3. The photostability of the sensitizer: material must be capable of many oxidation-reduction cycles without decomposition.

2.1. Operation principle

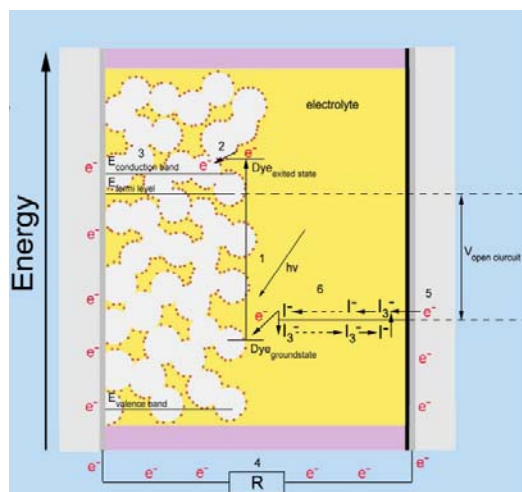


Fig. 2 Operation principle of a dye-sensitized solar cell

The operation principle of DSSC is displayed in Fig. 2. It can be divided in few following “steps”:

1. An electron is traced passing through a complete cycle of excitation
2. Injection in the TiO_2
3. Iodine reduction at the counter electrode and electron is passing to the electrode trough TiO_2
4. External work of electron
5. Diffusion in the electrolyte
6. Regeneration of the oxidized dye

During the first step the dye is excited by absorption of a photon. The most commonly used dye is a metal-organic type based on Ru or Mg, but also other types of dyes such as carotenoids were used for research. In conjunction with chlorophyll *a* as a sensitizer these were used as a redox spacer. It proved to increase the energy to electricity conversion efficiency (η) by 30% with the use of spirilloxanthin [10].

Majority of the dyes have an absorption onset in the range of 720 nm, so they are far from ideal dye parameters.

Natural organic dyes have absorption window in VIS spectra [11]. That is why organic dyes prepared by synthesis process have been successfully used in research. In case of a natural organic dye there has been effort to improve the overall efficiency of the cell by using two different dyes to complement each other. By using this synergistic effect for chlorophyll and xanthophyll dyes there was observed an increase in the energy to electricity conversion efficiency (η) of the mixture in comparison with a separate use of these dyes. Also an increase in P_{\max} was observed for the mixture compared to the linear superposition of the cells sensitized by individual pigments [12].

The lifetime of the excited state of the dye is in the nanosecond range. For the N3 (ruthenium complex *cis*- $\text{RuL}_2(\text{NCS})_2$ L=2,2'-bipyridyl-4,4'-dicarboxylic acid) dye, which renders one of the best photovoltaic performances, the characteristic lifetime is 60ns.

In the second step, the dye injects an electron into the conduction band of TiO_2 , ZnO or SnO_2 , which are also used in DSSC solar cells. The injection of the electrons may occur from the singlet state or the triplet state. In case of the singlet state the injection constants are in femtosecond range and by approximately one order of magnitude slower than for the triplet state [13, 14]. For efficient charge injection the energy level of the dye has to be above the TiO_2 conduction band edge. In case of the triplet state, the energy level is only slightly above the conduction band edge for TiO_2 , the electron injection driving force and electron transfer probability are low, therefore the triplet state has slow injection rate.

The charge injection occurs from the π^* -orbitals of the anchoring group to the titanium 3d orbitals. For efficient charge injection overlap of these orbitals is mandatory. As mentioned above injection of the electrons from the dye into the TiO_2 typically happens in femtosecond to picosecond time scale whereas charge recombination in the microsecond to millisecond time scale.

Precondition for an efficient charge injection is that the back reaction of a conduction band electron to the oxidized dye is much slower than the reduction of the oxidized dye by the electrolyte.

The reduction of oxidized sensitizer dye molecules occurs in the ms or μs range, which is by several orders of magnitude slower than injection rate. This difference is the main reason for the efficient charge separation in the DSSC device.

In the third step the electron passes through the nanoporous TiO_2 layer, which is a layer containing spherical anathase particles with a diameter between 20-30 nm. The material is weakly n-doped because of the oxygen vacancies in the lattice [15]. The thickness of the

layer is mostly in the range of 10 μm . The electrode contains about 10^{15} particles. As mentioned above the surface area is about 1000 times larger than the projected area. Conductivity and flat band potential are mainly determined by the surface. Dominant transport mechanism is diffusion of the electrons through the TiO_2 layer, because TiO_2 nanoparticles are small to build a macroscopic electric field. Transport of the electrons can be described by the trapping/detrapping model [16]. Since the diffusion is the only driving force, the diffusion length must be at least as long as the thickness of the TiO_2 electrode. For the thickness of the electrode of 10 μm , the efficient charge extraction lifetime of an electron is about 20 μs .

In the electrolyte reductions of triiodide occur by conduction band electrons.

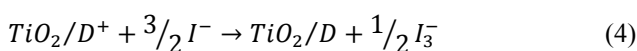
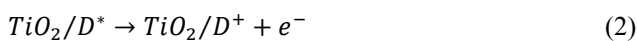
During the last three steps the following phenomena can be observed. First, the electron flows through the external circuit and performs work. Then at the counter electrode the electron is transferred into a hole conducting medium (electrolyte). In the most cases it is iodide/triiodide solution, but the investigation was done using the electrolyte of not liquid type, but of polymer type or sol-gel type.

For example, the sol-gel type electrolyte used by Štangar et al. showed the highest efficiency of 4.1% at immediate measurement and about half the value of the initial I_{sc} after few days, but U_{oc} remained unchanged [17]. Jilian Nei de Freitas used as an electrolyte poly(ethylene oxide) based derivative with no changes in the cell's efficiency observed after 30 days of solar irradiation (100 mW/cm^2) [18].

The reduction at the counter electrode is catalyzed by a thin layer of platinum or PEDOT:PSS.

In case of iodide/triiodide hole conductor electrolyte, which is widely used in DSSCs despite its disadvantages (necessity for sealing because the possibility of leakage, corrosive effects of iodide on contacts) the efficiency of DSSC is based on different rates for iodine reduction at the front and counter electrode. Iodine reduction on the counter electrode has to be orders of magnitudes faster than the recombination at the TiO_2 electrolyte interface.

The regeneration of the oxidized dye occurs in the nanosecond range [19]. It is 100 times faster than the recombination reaction and 10^8 times faster than the intrinsic lifetime of the oxidized dye. The chemical reactions, which take part in all the processes, can be described as follows:



where D represents dye sensitizer.

2.2. Typical DSSC performance

The performance of a solar cell is defined by parameters such as short-circuit current I_{sc} and open-circuit voltage V_{oc} obtained under standard illumination conditions (AM 1.5). Fill factor (FF) under standard conditions is a measure of the diode behaviour of the cell. It is obtained by full current-voltage characterization. The equation is:

$$FF = \frac{P_{max}}{V_{oc}I_{sc}} = \frac{(VI)_{max}}{V_{oc}I_{sc}} \quad (7)$$

The incident photon conversion efficiency (IPCE) is an incident energy-dependent quantity. It is a measure of the useful range of the cell. The IPCE is given by

$$IPCE = \frac{P_{in}}{I_{sc}} * \frac{e\lambda}{hc} \quad (8)$$

where λ is wavelength, P_{in} incident optical power, e is the fundamental electron charge, h Planck's constant and c is the speed of light in vacuum.

The global power conversion efficiency of energy to electricity conversion efficiency (η) of a cell with P_{out} electrical power under standard illumination conditions is given by

$$\eta = \frac{P_{out}}{P_{in}} = I_{sc}V_{oc} \frac{FF}{P_{in}} \quad (9)$$

In Fig. 3 is photocurrent-voltage curve obtained for a nanocrystalline TiO_2 solar cell sensitized by "black dye" - triscarboxy-ruthenium terpyridine [$\text{Ru}(4,4',4''\text{-(COOH)}_3\text{-terpy})(\text{NCS})_3$]. This system is efficient right into the low-frequency range of red and IR light. The wide spectral response results in the dye having a deep brown-black colour thus it is called "black dye" [20].

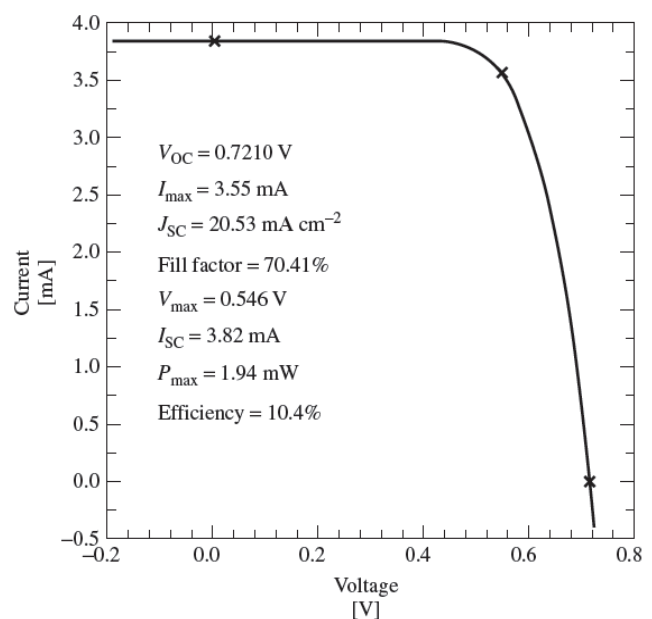


Fig. 3 Photocurrent-voltage curve obtained for a nanocrystalline TiO_2 solar cell sensitized by black dye. The results were obtained at the NREL calibration laboratory. (From Ref. 9)

3. CONCLUSION

The dye-sensitized nanocrystalline electrochemical photovoltaic cell in case of global power conversion efficiency of energy to electricity conversion efficiency (η) and cost needed to manufacture such cell has been proven to be serious competitor to today widely used conventional solar systems. By interchanging ITO semiconductor glass for optically active polymer the dye-sensitized solar cell can be made flexible and thinner. Such solar cells can be incorporated to places not suitable for conventional semiconductor solar cells. With lower thickness, weight and possibility to use a dye with various colours, polymer based dye-sensitized solar cells or glass type dye-sensitized solar cells can be used for fashion architecture, or fashion design.

ACKNOWLEDGMENTS

The work was supported by the Agency for Promotion of Research and Development, projects No. APVV-0362-07 and APVV-0290-06. This publication originates from the project "National Center for Research and Applications of Renewable Energy Sources" (IMTS 26240120016) of Operational program Research and Development financed by European fund of Regional Development.

REFERENCES

- [1] WEST, W.: *Proceedings of Vogel Centennial Symposium, Photogr. Sci.*, Eng. 18,35, 1974.
- [2] GERISHER, H. – TRIBUTSCH, H.: *Ber. Bunsen. Phys. Chem.* 72, pp. 437-445, 1968.
- [3] TRIBUTSCH, H. – GERISHER, H.: *Ber. Bunsen. Phys. Chem.* 73, pp. 251-260, 1969.
- [4] O'REGAN, B. – GRÄTZEL, M.: *Nature*, 353, pp. 737-740, 1991.
- [5] VENZ, P. A. – KLOPROGGE, J. T. – FROST, R. L.: *Langmuir*, 16(11), pp. 4962-4968, 2000.
- [6] WILSON, G. J. – WILL, G. D. – FROST, R. L. – MONTGOMERY, S. A.: *J. Mat. Chem.*, 12, pp. 1787-1791, 2002.
- [7] GRÄTZEL, M.: *Nature*, 414, pp. 338-344, 2001.
- [8] GRÄTZEL, M.: *J. Photochem. Photobiol. C: Photochem. Reviews*, 4, pp. 145-153, 2003.
- [9] HAGGELDT, A. – GRÄTZEL, M.: *Acc. Chem. Res.*, 33, pp. 269, 2000.
- [10] WANG, X. F. – XIANG, J. – WANG, P. – KOYAMA, Y.: Dye-Sensitized Solar Cells using chlorophyll *a* derivative as the sensitizer and carotenoids having different conjugation lengths as redox spacers, *Science Direct: Chem. Phys. Lett.*, 408, pp. 409-414, 2005.
- [11] ASOK, K. JANA: Solar cells based on dyes Review, *J. Photochem. Photobiol. A: Chem*, 132, pp. 1-17, 2000.
- [12] LIU, B. – ZHAO, X. – LUO, W.: The synergistic effect of two photosynthetic pigments in dye-sensitized mesoporous TiO₂ solar cells, *Science Direct: Dyes and Pigments*, 76, pp. 327-331, 2008.
- [13] TACHIBANA, Y. – MOSER, J. E. – GRÄTZEL M. – KLUG, D. R. – DURRANT, J. R.: *J. Phys. Chem.*, 100, 20056, 1996.
- [14] ASHBURY, J. B. – ELLINGTON, R. T. – GOSH, H. – FERRERE, S. – NOZIK, A. J. – LIAN, T.: *J. Phys. Chem. B.*, 103, 3110, 1999.
- [15] CHEUNG, S. H. et al.: N incorporation and electronic structure in N-doped TiO₂(1 1 0) rutile, *Science Direct: Surface Science* 601, Issue 7, pp. 1754-1762, 2001.
- [16] FISHER, A. C. et al.: Intensity Dependence of the Back Reaction and Transport of Electrons in Dye-Sensitized Nanocrystalline TiO₂ Solar Cells, *J. Phys. Chem. B*, 104 (5), pp 949–958, 2000.
- [17] ŠTANGAR, U. L. et al.: A Sol-Gel Type of Electrolyte for a Dye-Sensitized Solar Cell: Attenuated Total Reflectance (ATR) Vibrational Spectra Studies, *J. Sol-Gel Science and Tech.*, 26, pp. 1113-1118, 2003.
- [18] FREITAS, J. N. – NOGUEIRA, V. C. – ITO, B. I. et al.: Dye-sensitized solar cells and solar module using polymer electrolytes: Stability and performance investigations, *International Journal of Photoenergy*, vol. 2006, 2006.
- [19] HILGENDORFF, M. – SUNDSTRÖM, V.: Dynamics of Electron Injection and Recombination of Dye-Sensitized TiO₂ Particles, *J. Phys. Chem. B*, 102 (51), pp. 10505–10514, 1998.
- [20] Dye Sensitized Solar Cells (DYSC) based on Nanocrystalline Oxide Semiconductor Films. *Laboratory for Photonics and Interfaces, École Polytechnique Fédérale de Lausanne*. 2 February 1999. <http://lpi.epfl.ch/solarcellE.html>.

Received March 6, 2010, accepted July 12, 2010

BIOGRAPHIES

Michal Sokolský was born on 10.8.1983. In 2007 he graduated (MSc) at the department of Physics of the Faculty of Electrical Engineering and Informatics at Slovak Technical University in Bratislava. His thesis title was "Langmuir layers of chlorophyll *a*: model systems of photosynthesis". Since 2007 he has been studying as PhD. student at the Department of Physics. His scientific research is focused on organic thin film technologies and organic photovoltaics.

Július Cirák was born on the 29th June 1953 in Likier. He graduated from the Faculty of Electrical Engineering, Slovak University of Technology, Bratislava, in 1976, and received the CSc (PhD) degree in experimental physics in 1981. He joined the Department of Physics at the same faculty, as an Assistant (1982), Associate (1988) and Full Professor (2008). His research experience and interest includes: organic molecular thin layer systems and nanostructures, technology, study of electrical and optical properties and applications for organic electronics.