

Brief Overview of Dye-Sensitized Solar Cells

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Abstract Dye-sensitized solar cells (DSC) are based on molecular and nanometer-scale components. Record cell efficiencies of 12%, promising stability data and means of energy-efficient production methods have been accomplished. As selling points for the DSC technology the prospect of low-cost investments and fabrication are key features. DSCs offer the possibilities to design solar cells with a large flexibility in shape, color, and transparency. The basic principles of the operation of DSC, the state-of-the-art as well as the potentials for future development are described.

Keywords Dye-sensitized · Solar cell · Mesoporous · Photoelectrochemistry · Nanostructured

INTRODUCTION

The umbrella of solar-energy conversion encompasses solar thermal, solar fuels, solar-to-electricity (photovoltaic, PV) technology, and the great many subcategories below those. PVs, or solar cells, are fast growing both with regards to industrialization and research. Globally, the total PV installation is around 40 GW, and an annual growth rate of 45% has been experienced over recent years. Solar cell technologies can be divided into three generations. The first is established technology such as crystalline silicon. The second includes the emerging thin-film technologies that have just entered the market, while the third generation covers future technologies that are not yet commercialized. A useful link for PV updates is www.solarbuzz.com. For a review of PV technologies with special emphasis on the materials science aspects we refer to Gibson and Hagfeldt (2011).

When comparing different PV technologies, a figure of merit is the production cost per peak watt of solar

electricity produced. For so-called second-generation thin-film solar cells, production costs below $\$1/W_{\text{peak}}$ are reported. To be competitive for large-scale electricity production, new PV technologies thus need to aim at production costs down to, and even below, $\$0.5/W_{\text{peak}}$. To give an example, this means a cost of 70 $\$/\text{m}^2$ at a module efficiency of 14%. The dye-sensitized solar cell (DSC) is a molecular solar cell technology that has the potential to achieve production costs below $\$0.5/W_{\text{peak}}$.

DSC is based on molecular- and nanometre-scale components. Record cell efficiencies of 12%, promising stability data and energy-efficient production methods, have been accomplished. In the present table of record solar cell efficiencies (Green et al. 2011), in which the solar cell area must be at least 1 cm^2 , the record is held by the Sharp company in Japan at 10.9%. The record for a DSC module is 9.9% achieved by Sony, Japan. As selling points for the DSC technology, the prospect of low-cost investments and fabrication and short energy-payback time (<1 year) are key features. DSCs offer the possibilities to design solar cells with a large flexibility in shape, color, and transparency. Integration into different products opens up new commercial opportunities for niche applications. Ultimately, the comparison of different energy sources is based on the production cost per kWh, i.e., the cost in relation to energy production. For DSC technology, it is advantageous to compare energy cost rather than cost per peak watt. DSCs perform relatively better compared with other solar cell technologies under diffuse light conditions and at higher temperatures.

DSC research groups have been established around the world and the field is growing fast, which can be illustrated by the fact that about two or three research articles are being published every day. From a fundamental research point of view, we can conclude that the physical chemistry

of several of the basic operations in the DSC device remains far from fully understood. For specific model and reference systems and controlled conditions, there is a rather detailed description in terms of energetics and kinetics. It is, however, still not possible to predict accurately how a small change to the system—e.g., replacing one component or changing the electrolyte composition—will affect DSC performance. With time, the chemical complexity of DSCs has become clear, and the main challenge for future research is to understand and master this complexity, in particular at the oxide–dye–electrolyte interface. A challenging but realizable goal for the present DSC technology is to achieve efficiencies above 15%. We have for many years known where the main losses in the state-of-the-art DSC device are, i.e., the potential drop in the regeneration process of the photo-oxidized dye with the electrolyte, and the recombination loss between photo-injected electrons in the mesoporous TiO_2 electrode and the electrolyte (Fig. 1). With our breakthrough of using one-electron transfer redox systems such as Co-complexes, in combination with a dye, which efficiently prevents the recombination loss, we may now have found the path to increase the efficiency significantly (Feldt et al. 2010). With the recent world record of 12.3 by Grätzel and co-workers (Yella et al. 2011) using Co-complexes, the main direction of the research field is now to explore this path.

The industrial interest in DSCs is strong and several companies present encouraging results, in particular with regard to upscaling with world record minimodule efficiencies above 9% (Sony and Fujikura). In this context, we

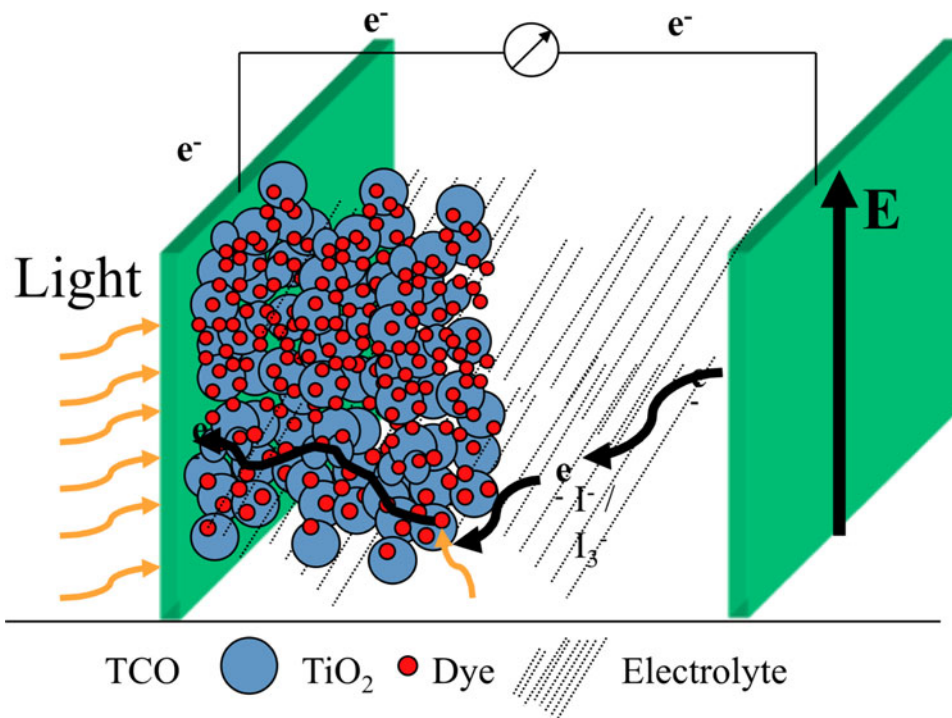
note that world record efficiencies are not the same as stable efficiencies obtained after durability tests. Reported stable module efficiencies vary significantly in the literature and are difficult to judge. Best values in the literature are about 5%, although presentations at conferences report better results. Several companies are dedicated to setting up manufacturing pilot lines. G24i is a company based in Cardiff, Wales that focuses on consumer electronics. On its Web site (www.g24i.com), such niche products are now for sale. Companies that sell material components, equipment, and consultancy services have increased and are growing.

There are several recent reviews on DSCs, and the reader is referred to these papers for further information (Hagfeldt and Grätzel 1995, 2000; Grätzel 2001, 2005, 2009; Bisquert et al. 2004; Peter 2007a, b; Ardo and Meyer 2009; O'Regan and Durrant 2009; Hagfeldt et al. 2010; Kalyanasundaram 2010; Meyer 2010).

OVERVIEW OF CURRENT STATUS AND OPERATIONAL PRINCIPLES

Since the initial work in the beginning of the 1990s by O'Regan and Grätzel (1991), many DSC components and configurations have been developed. At present, several thousands of dyes have been investigated. Fewer, but certainly hundreds of electrolyte systems and mesoporous films with different morphologies and compositions have been studied and optimized. A schematic of the interior of a DSC showing the principle of how the device operates is shown in Fig. 1.

Fig. 1 A schematic of the interior of a DSC showing the principle of how the device operates



The typical configuration is as follows. At the heart of the device is the mesoporous oxide layer composed of a network of TiO_2 nanoparticles, which have been sintered together to establish electronic conduction. The layer is in the sintering step also deposited on a transparent conducting oxide (TCO) substrate forming an ohmic contact. Typically, the mesoporous film thickness is ca. 10 μm and the nanoparticle size 10–30 nm in diameter; the porosity is 50–60%. The mesoporous layer is deposited on a TCO on a glass or plastic substrate.

Attached to the surface of the nanocrystalline film is a monolayer of the charge-transfer dye. The state-of-the-art dyes have since the breakthrough of DSC in 1991 been based on ruthenium complexes. Several other dye families, such as porphyrines and different types of purely organic dyes, have been catching up and show today similar performances as the best Ru-complexes. Photoexcitation of the dye results in the injection of an electron into the conduction band of the oxide leaving the dye in its oxidized state. The dye is restored to its ground state by electron transfer from the electrolyte, usually an organic solvent containing the iodide–triiodide redox system. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The I_3^- ions formed by oxidation of I^- diffuse a short distance (<50 μm) through the electrolyte to the cathode, which is coated with a thin layer of platinum catalyst where the regenerative cycle is completed by electron transfer to reduce I_3^- to I^- . For a DSC to be durable for more than 15 years outdoors, the required turnover number is 10^8 , which is satisfied by the best performing ruthenium complexes.

The voltage generated under illumination corresponds to the difference between the electrochemical potential of the electron at the two contacts, which for DSCs is generally the difference between the Fermi level of the mesoporous TiO_2 layer and the redox potential of the electrolyte. Overall, electric power is generated without permanent chemical transformation.

As mentioned above, a huge number of material components, dyes, mesoporous and nanostructured electrodes, electrolytes, and counterelectrodes have been synthesized and developed for DSC applications. The material component variations of a DSC device are therefore endless. It is important to keep in mind that the description above, and the one below in the next section, of the conventional DSC device with a mesoporous TiO_2 , a Ru-complex sensitizer, I^-/I_3^- redox couple, and a platinized TCO counterelectrode is only valid for this particular combination of material components. As soon as one of these components are modified or completely replaced by another component, the picture has changed; energetics and kinetics are

different and need to be determined for the particular system at hand. To generalize a result in DSC research is therefore difficult and can many times be misleading.

CENTER FOR MOLECULAR DEVICES, SWEDEN, AND A RECENT BREAKTHROUGH FOR DYE-SENSITIZED SOLAR CELLS

The research constellation Center for Molecular Devices (CMD) has become one of the world leading scientific centers for DSC research. Our recent contribution for a review of the DSC field is found in Hagfeldt et al. (2010).

From a fundamental point of view DSC has seen a real breakthrough during 2011 thanks to the work of CMD. For the first time since the famous Nature paper by O'Regan and Grätzel (1991) it has been possible to replace the iodide/tri-iodide redox couple with a one-electron redox system based on cobalt complexes. The success comes from our collaborations within CMD, leading to the development of the D35 dye and Co-complex based electrolytes (Feldt et al. 2010), see Fig. 2.

The background to this breakthrough is that the standard redox electrolyte for DSC has, ever since the very start in 1991, been the iodide–triiodide (I^-/I_3^-) redox couple in an organic solvent. It has good solubility and a suitable redox potential, and it provides rapid dye regeneration. A serious disadvantage of this redox mediator is that a significant part of the potential is lost in the regeneration of the oxidized dye due to intermediate reactions. To develop DSC with efficiencies significantly larger than 12%, our strategy was to use one-electron redox couples or hole conductors instead of I^-/I_3^- . Unfortunately, the use of one-electron mediators in DSC nearly always leads to strongly increased recombination between electrons in TiO_2 and the oxidized part of the redox couple, which seriously limits the solar cell efficiency. Recently, however, we obtained a breakthrough with cobalt polypyridine-based mediators in combination with the organic dye, D35. Careful matching of the steric bulk of the mediator and the dye molecules minimizes the recombination between electrons in TiO_2 and Co(III) species in the electrolyte and avoids mass transport limitations of the redox mediator. The organic sensitizer D35, equipped with bulky alkoxy groups, efficiently suppresses recombination, allowing the use of cobalt redox mediators with relatively small steric bulk. Based on these concepts Grätzel and co-workers published, in November 2011, the new DSC efficiency world record of 12.3% (Yella et al. 2011). The record cell is based on a Co-complex redox electrolyte in combination with two co-sensitizing dyes (a porphyrin and an organic dye) facilitated with alkoxy steric groups.

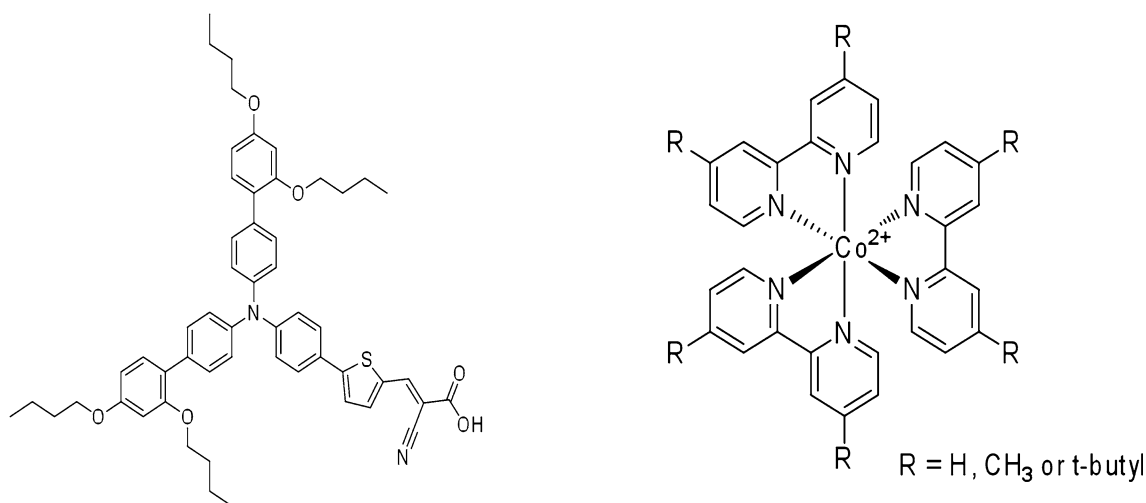


Fig. 2 Structure of the organic dye, D35, and Co-complexes as redox mediators

FUTURE OUTLOOK

With time, the chemical complexity of DSCs has become clear, and the main challenge for future research is to understand and master this complexity, in particular at the oxide–dye–electrolyte interface. Thus, for future research, it will be important to carefully select several reference systems that emphasize different key aspects of the device and characterize these systems in depth with all the different techniques we have at hand. From comparisons and modeling, we may then find a better generality of our fundamental understanding.

A challenging but realizable goal for the present DSC technology is to achieve efficiencies above 15%. The new one-electron-based redox couples may significantly lower the voltage drop between the redox system and the oxidized dye, thus pointing out the direction to reach above 15%. This will require electron-transfer studies to clarify how much driving force is needed in the regeneration step and how this can be optimized by tuning of the redox potential by modification of the redox complexes and the oxidation potential of the dye. Moreover, the blocking of the recombination reaction of electrons in the oxide with electrolyte species is an important task for further design of dye molecules and surface passivation methods.

Regarding stability of DSC cells and modules, the conditions for accelerated testing have not yet been standardized. Until now, 1000-h light-soaking and 1000-h high-temperature storage tests have mainly been performed to compare materials and to show feasibility of the technology. As the technology advances, the outcome of accelerated testing will also be used to start calculating acceleration factors and estimating product life. Since this is not straightforward, intensified research and development is urgently required to define the procedures for

relevant accelerated testing of dye-sensitized solar devices. Especially important is collecting outdoor test results from different locations and application-relevant conditions. The outcome needs to be related to results from accelerated testing to define the key tests for accelerated testing of DSC modules.

For the DSC technology, it is advantageous to compare energy cost rather than cost per peak watt. DSCs perform relatively better compared with other solar cell technologies under diffuse light conditions and at higher temperatures. An overall goal for future research will thus be to collect data and develop models to make fair judgments of the DSC technology with regards to energy costs.

With the ever-increasing industrial development of the DSC technology, we anticipate some exciting years to come with possible introduction of niche applications such as consumer electronics and successful development of manufacturing processes.

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REFERENCES

- Ardo, S., and G.J. Meyer. 2009. Photodriven heterogeneous charge transfer with transition-metal compounds anchored to TiO₂ semiconductor surfaces. *Chemical Society Reviews* 38: 115–164.
- Bisquert, J., D. Cahen, G. Hodes, S. Ruhle, and A. Zaban. 2004. Physical chemical principles of photovoltaic conversion with nanoparticulate, mesoporous dye-sensitized solar cells. *Journal of Physical Chemistry B* 108: 8106–8118.
- Feldt, S.M., E.A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, and A. Hagfeldt. 2010. Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells. *Journal of the American Chemical Society* 132: 16714–16724.

- Gibson, E.A., and A. Hagfeldt. 2011. Solar energy materials. In *Energy materials*, Chap. 3, eds. D.W. Bruce, D. O'Hare, and R. Walton. Chichester: Wiley. ISBN 978-0-470-99752-9.
- Grätzel, M. 2001. Photoelectrochemical cells. *Nature* 414: 338–344.
- Grätzel, M. 2005. Solar energy conversion by dye-sensitized photovoltaic cells. *Inorganic Chemistry* 44: 6841–6851.
- Grätzel, M. 2009. Recent advances in sensitized mesoscopic solar cells. *Accounts of Chemical Research* 42: 1788–1798.
- Green, M.A., K. Emery, Y. Hishikawa, and W. Warta. 2011. Solar cell efficiency tables (Version 38). *Progress in Photovoltaic* 19: 565–572.
- Hagfeldt, A., and M. Grätzel. 1995. Light-induced redox reactions in nanocrystalline systems. *Chemical Reviews* 95: 49–68.
- Hagfeldt, A., and M. Grätzel. 2000. Molecular photovoltaics. *Accounts of Chemical Research* 33: 269–277.
- Hagfeldt, A., G. Boschloo, L. Sun, L. Klöö, and H. Pettersson. 2010. Dye-sensitized solar cells. *Chemical Reviews* 110: 6595–6663.
- Kalyanasundaram, K. 2010. *Dye-sensitized solar cells*, 1st ed. Lausanne: EPFL Press. ISBN 978-2-940222-36-0.
- Meyer, G.J. 2010. The 2010 millennium technology grand prize: Dye-sensitized solar cells. *ACS Nano* 4: 4337–4343.
- O'Regan, B.C., and J.R. Durrant. 2009. Kinetic and energetic paradigms for dye-sensitized solar cells: Moving from the ideal to the real. *Accounts of Chemical Research* 42: 1799–1808.
- O'Regan, B., and M. Grätzel. 1991. A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO₂ films. *Nature* 353: 737–740.
- Peter, L.M. 2007a. Characterization and modeling of dye-sensitized solar cells. *Journal of Physical Chemistry C* 111: 6601–6612.
- Peter, L.M. 2007b. Dye-sensitized nanocrystalline solar cells. *Physical Chemistry Chemical Physics* 9: 2630–2642.
- Yella, A., H.-W. Lee, H.N. Tsao, C.Y. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, et al. 2011. Porphyrin-sensitized solar cells with Cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science* 334: 629–634.

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