

# Photoelectrochemical Cells Based on Dye Sensitization for Electricity and Fuel Production

Nick Vlachopoulos and Anders Hagfeldt\*

**Abstract:** Dye-sensitized semiconductor oxide photoelectrodes in which light is absorbed by a monomolecular layer of dye chemisorbed on a porous oxide substrate have attracted considerable interest in the last 35 years, mainly for the conversion of sunlight to electricity, in dye-sensitized solar cells (DSSCs) with maximal efficiencies in the range 10–15%, and, most recently, as dye-sensitized photoelectrochemical cells (DSPECs) for the generation of solar fuels. In the latter direction, considerable progress has been achieved but the efficiency is notably lower than for electricity generation. In the present review, the basic physicochemical principles of the DSSC and DSPEC operation are described, several keynote results reported, and the factors limiting the performance and necessitating further research highlighted.

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



**Nick Vlachopoulos** obtained a degree in chemical engineering from the National Technical University of Athens, Greece (1979), and two doctorates from the University of Pennsylvania, PA, USA (1984), and the Swiss Federal Institute of Technology in Lausanne (EPFL), Switzerland (1990). He worked as researcher in the group of Professor Michael Grätzel at EPFL (1986–1999). Later, he was

employed in Denmark, Germany, Sweden, and Ireland. In 2014, he returned to EPFL as Senior Research Scientist and Lecturer in the group of Professor Anders Hagfeldt. His activities are related to the molecular electrochemistry of chemically modified mesoporous oxide electrodes and their application to solar energy.



**Anders Hagfeldt** is Professor of Physical Chemistry at the Swiss Federal Institute of Technology in Lausanne (EPFL). He obtained his PhD degree from Uppsala University in 1993 and was a postdoctoral fellow with Professor Michael Grätzel (1993–1994) at EPFL. His research focuses on the fields of dye-sensitized solar cells, perovskite solar cells, and solar fuels.

According to Web of Science, July 2019, he has published more than 510 scientific papers that have received over 60000 citations (h index of 117). From 2014 to 2018, he was on the list of Thomson Reuter's Highly Cited Researchers. He is a member of, for example, the Royal Swedish Academy of Sciences, Stockholm, and the Royal Swedish Academy of Engineering Sciences. He is Doctor Honoris Causa at Paris Diderot University, France.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have been established in the last quarter-century as a promising third-generation solar cell technology. First-generation solar cells include a number of well-known types like monocrystalline silicon. Recently commercialized thin-film solar cells, like cadmium indium gallium selenide (CIGS) belong to the second generation. New types of solar cells not yet commercialized, including, in addition to DSSCs, quantum-dot solar cells and organic bulk heterojunction solar cells comprise the third category. An overview of the various solar cell types has been published by Gibson and Hagfeldt.<sup>[1]</sup>

In DSSCs the light-absorbing element is a monomolecular dye layer adsorbed on a porous, high-surface semiconductor substrate. The highest not certified sunlight-to-electricity energy conversion efficiency is 14%.<sup>[2]</sup> The highest certified efficiency, according to the present table of record solar efficiencies, including data obtained with devices with surface area of 1 square centimetre or larger, is 11.9% for a cell, 10.7% for a minimodule and 8.8% for a module, all of them obtained by Sharp, Japan.<sup>[3]</sup> The advantages of DSSCs compared with existing technology include lower production cost, possibility of preparation in flexible substrates, transparency and variability of colour. In the initial period of the DSSC research and development, in the early 1990s, a key proposed advantage was the huge difference in cell production cost as compared with crystalline solar cells. In the meantime, the latter cost has been substantially reduced so that the current emphasis is in niche applications, for example building-integrated photovoltaics and indoor applications. In the latter case, it should be noted that the DSSCs have been proven to exhibit a higher efficiency under low light intensity, direct or diffuse. An additional advantage of DSSCs is that their performance does not decline at higher temperatures.

The basic physicochemical processes related to DSSC operation are understood, however, several details have to be elucidated. Particular challenges are posed by the properties of the low-conductivity nanostructured substrate, related to the development of novel theoretical concepts. The goal of continuing re-

\*Correspondence: Prof. A. Hagfeldt, E-mail: Anders.Hagfeldt@epfl.ch

Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, School of Basic Sciences, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

search in several related fields of science is to be able to rationally adjust the properties of the various components, including the dye, the oxide substrate, the redox mediator or solid-state hole conductor effecting the charge transport between photoelectrode and dark counter electrode within the DSSC, various additives in the charge-transport medium contributing to the enhancement of the photocurrent or the suppression of the dark current, catalytic counter electrode, and antireflective coatings, so as to optimize the DSSC performance in conjunction to the particular requirements of the intended application. At present the target of DSSC research is to enhance the sunlight-to-electricity efficiency to above 15% and, at the same time, with simultaneous long-term stability under continuous full-sun simulated sunlight for a period in the range of 1'000–10'000 hours.

In this respect, the pathway first initiated during the early 1990s by Anders Hagfeldt, Licheng Sun and co-workers in Sweden, involved the combination of a one-electron cobalt II/III coordination complex as redox mediator, characterized by fast electron transfer, and a metal-free organic dye.<sup>[4]</sup> A particular feature of the latter was that it contained surface-active groups at the periphery of the molecule which contributes to the suppression of the dark recombination current associated with the reduction of the mediator, flowing to the opposite direction of that of the photocurrent and seriously limiting the efficiency. These initial investigations introduced a reorientation of DSSC research towards the replacement of iodide-triiodide by other mediators and the development of dyes compatible with them. The recently obtained record of efficiency by Hanaya and collaborators<sup>[2]</sup> is an outgrowth of this activity.

The progress attained in DSSCs is described in several review publications: Hagfeldt and Grätzel,<sup>[5,6]</sup> Grätzel,<sup>[7,9,13]</sup> Bisquert *et al.*,<sup>[8]</sup> Peter,<sup>[10,11]</sup> Ardo and Meyer,<sup>[12]</sup> O'Regan and Durrant,<sup>[14]</sup> Hagfeldt *et al.*,<sup>[15]</sup> Kalyanasundaram,<sup>[16]</sup> Meyer,<sup>[17]</sup> Freitag and Boschloo,<sup>[18]</sup> Benesperi *et al.*,<sup>[19]</sup> Vlachopoulos *et al.*<sup>[20]</sup>

In addition to the conversion of light to electricity in regenerative DSSCs, without a net modification of the electrolyte composition, the generation of fuels at the illuminated semiconductor–electrolyte interface has attracted increased interest since the 1970s, following the pioneer research of Fujishima and Honda,<sup>[21–24]</sup> with emphasis on photoelectrochemical cells (PECs) based on the direct photoexcitation of semiconductors. After the success of dye-sensitized electrodes in DSSC the possibility of their use for generation of fuel or other useful molecules has been systematically studied in the last twenty years. Important insights as regards the mechanism of photooxidation and photoreduction reactions on dye-coated electrodes, in conjunction with the introduction of novel catalytic systems,<sup>[25–76]</sup> have been obtained. However, the best solar energy conversion efficiencies achieved in such dye-sensitized photoelectrochemical cell systems are two orders of magnitude lower compared to DSSCs. PECs based on dye-sensitized electrodes are termed dye-sensitized photoelectrochemical cells (DSPECs). Strictly speaking, the term dye-sensitized photoelectrochemical cell should encompass both the generation of electricity and chemicals, since in both cases electrochemical reactions are involved at the interface between an electronic and an ionic conductor, analogous to the case of photoelectrochemical cells based on the direct photoexcitation of semiconductors. However, in the current literature the designation DSPECs for the sensitized devices generating chemicals is well entrenched, while the term DSSC indicates a dye-sensitized electrochemical photovoltaic cell for electricity generation.

## 2. Overview of Current Status and Operational Principles

The initial research in the Grätzel laboratory and elsewhere and other researchers in the second half of the 1980s and the first half of the 1990s on efficient high-surface area dye-sensitized TiO<sub>2</sub> electrodes at first and DSSCs subsequently,<sup>[77–85]</sup> was fol-

lowed in the last quarter-century by extensive investigations on several DSSC components and cell types. Initially the main efforts were dedicated to dye optimization. A large number of dyes were investigated, with emphasis initially on ruthenium coordination complexes, profiting from the substantial progress achieved in inorganic coordination chemistry and inorganic photochemistry, and later in organic metal-free dyes. In parallel, less extensive but significant efforts were dedicated to the optimization of the mediator-electrolyte charge transport medium, or the alternative option of a solid-state inorganic or organic hole conductor as charge-transport medium, the nature of the mesoporous film and several thousands of dyes have been investigated.

A typical DSSC system is illustrated in Fig. 1. The photoelectrode is based on a mesoporous semiconductor oxide, mainly TiO<sub>2</sub>, nanoparticulate layer, of thickness around 5–10 nm, with typical particle size of 10–30 nm. The film is deposited on a glass or polymer substrate coated with a transparent conducting oxide (TCO) film, commonly F-doped tin oxide (FTO), or in some cases tin-doped indium oxide (indium tin oxide, ITO). The transparency of the substrate allows for irradiation from the back of the photoelectrode. For some applications the dye/porous oxide layer can be deposited on a titanium or iron foil, in which case the incident light impinges from the electrolyte side of the photoelectrode: in this case a sufficiently transparent counter electrode is needed.

The monomolecular layer of the dye is chemisorbed, by means of either covalent attachment or hydrogen bond formation. In both cases, surface groups, *e.g.* Ti–OH or Ti–O–Ti assume an essential role.

Upon irradiation with light of suitable wavelength an electron is excited to the lowest lying unoccupied molecular orbital (LUMO), with an electron vacancy left to the highest lying occupied molecular orbital (HOMO). The excited dye undergoes oxidation by injecting an electron into the semiconductor conduction band. The oxidized dye reverts to the initial form by accepting an electron from the reduced form of a redox mediator. The mediator diffuses in the electrolyte toward the counter electrode, getting available for reoxidation.

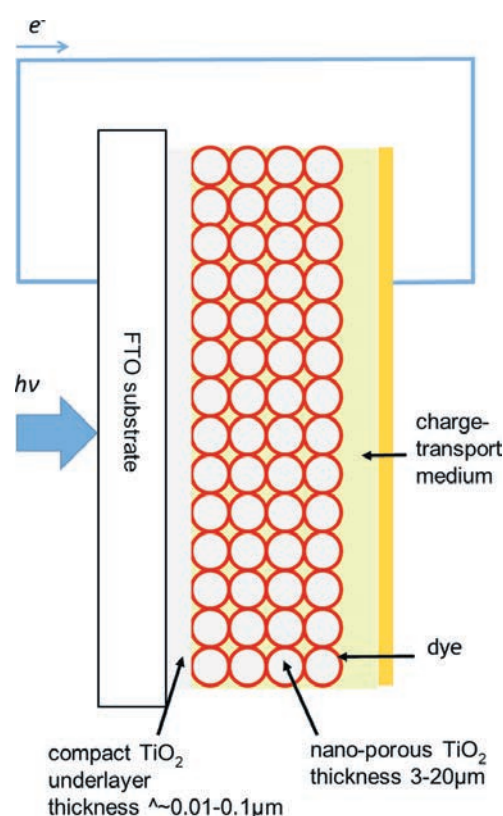


Fig. 1. Configuration of a dye-sensitized solar cell. Adapted from Vlachopoulos *et al.*, 2015,<sup>[20]</sup> copyright Swiss Chemical Society.

The photoexcited electrons are transferred to the photoelectrode contact (TCO or metal) and from there, through the external circuit, to the counter electrode, where they effect the oxidation of the reduced mediator. The latter diffuses back toward the photoelectrode in order to participate to a new photoexcitation-electron injection-regeneration cycle.

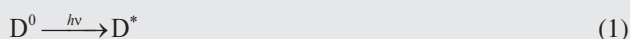
A stable dye-mediator system should be able to repeat this cycle several times. The number of such cycles is termed turnover number. For a ruthenium dye and the iodide-triiodide redox system a turnover number of  $10^8$  has been demonstrated, corresponding to DSSC operation under ambient, outdoor conditions for 15 years.

### 3. Charge Transfer and Charge Transport Processes; Regeneration, Recombination, Mass Transport and Counter Electrodes

The processes involved in the functioning of a DSSC can be categorized as either useful (Fig. 2) or deleterious (Fig. 3). The former lead to the efficient conversion of light to electricity, the latter hinder the DSSC performance. In the following description, the case of a dye-sensitized n-type semiconductor will be considered.

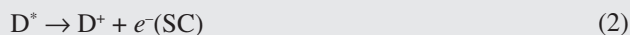
#### 3.1 Useful Processes

(a1) Dye photoexcitation:



where  $D^0$  is the reduced ground state and  $D^*$  is the reduced excited state of the dye.

(b1) Electron injection into the conduction band semiconductor oxide support (SC):



where  $D^+$  is the oxidised state of the dye. The superscripts 0 and + indicate relative charges and not the absolute charges of the species.

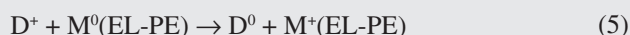
(c1) Electron transfer (collection) from the semiconductor to its conductive support (e.g. TCO) and then to the conductive contact phase with the external circuit ( $CT_{PE}$ ):



The contact between TCO and  $CT_{PE}$  is supposed to be ohmic so that the respective Fermi levels are equal:

$$E_F(TCO) = E_F(CT_{PE}) \quad (4)$$

(d1) Dye regeneration by redox reaction with the reduced form of the redox mediator  $M^0$ :



where  $M^+$  is the oxidized mediator and EL-PE is the electrolyte at the proximity of the photoelectrode. The standard Gibbs energy for the dye regeneration is formulated in terms of either a difference of standard Fermi levels or of standard redox potentials:

$$\begin{aligned} \Delta G_{reg}^0 &= N_A [E_F^0(D^+/D^0) - E_F^0(M^+/M^0)] \\ &= -F[E^0(D^+/D^0) - E^0(M^+/M^0)] \end{aligned} \quad (6)$$

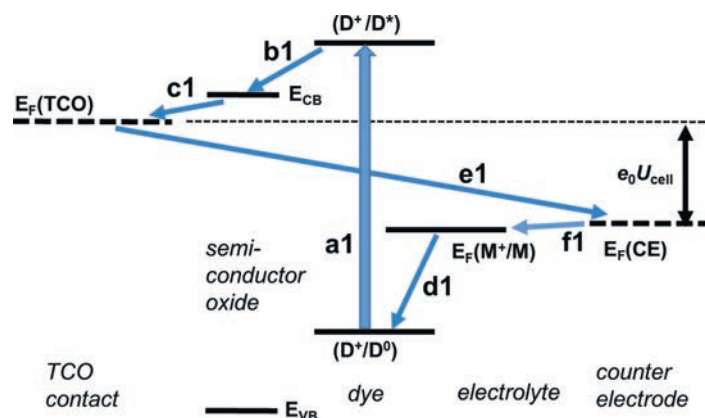
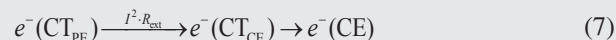


Fig. 2. Useful processes in a DSSC cell. The notation a1-f1 is explained in the text. The mass-transport processes are not shown. Adapted from Vlachopoulos *et al.*, 2015,<sup>[20]</sup> copyright Swiss Chemical Society.

where  $N_A$  is the Avogadro number.  $-\Delta G_{reg}^0$  is often termed the standard driving force of the dye regeneration.

(e1) Electron flow from the photoelectrode contact to the counter electrode contact through the external circuit and then to the counter electrode electronic conductor:



where  $(I^2 \cdot R_{ext})$  is the electrical energy output for current  $I$  and external resistance  $R_{ext}$ , corresponding to a cell voltage of

$$U_{cell} = IR_{ext} \quad (8)$$

The contact between CE and  $CT_{CE}$  is ohmic so that

$$E_F(CT_{CE}) = E_F(CE) \quad (9)$$

and the difference between the Fermi levels at the two contacts is

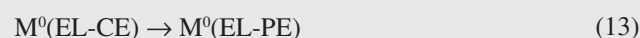
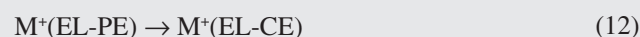
$$E_F(CT_{PE}) - E_F(CT_{CE}) = e_0 U_{cell} = e_0 IR_{ext} \quad (10)$$

Equivalently, by considering the ohmic contacts FTO/ $CT_{PE}$  and CE/ $CT_{CE}$

$$E_F(FTO) - E_F(CE) = e_0 U_{cell} = e_0 IR_{ext} \quad (11)$$

where  $e_0$  is the electron charge.

(f1) Mass transport processes of  $M$  and  $M^+$  in the electrolyte between PE and CE



where EL-CE is the electrolyte at the proximity of the counter electrode. By summing Eqns (1)–(11) it becomes evident that the net result is the conversion of light to electricity without any net change in the electrolyte or the electrodes.

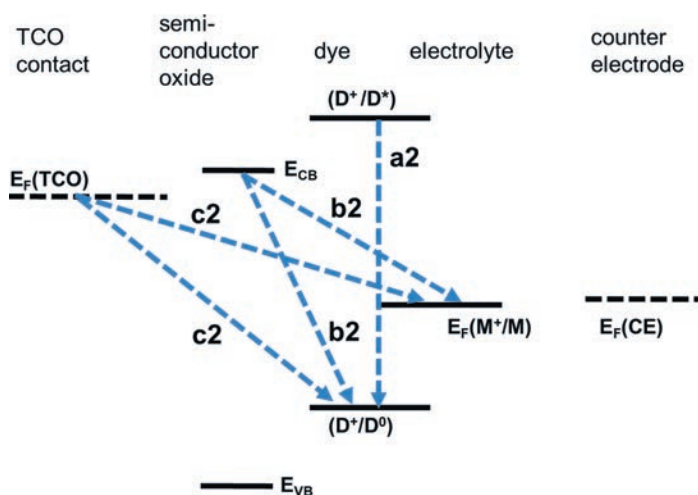
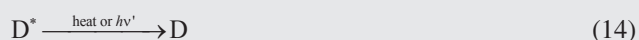


Fig. 3. Deleterious processes in a DSSC cell. The notation a2-c2 is explained in the text. Adapted from Vlachopoulos *et al.*, 2015,<sup>[20]</sup> copyright Swiss Chemical Society.

### 3.2 Deleterious Processes

(a2) Deactivation of the dye excited state with evolution of light (luminescence) or heat:



resulting to the evolution of heat or luminescent light, with the frequency  $\nu'$  in general different from that of the impinging light.

(b2) Recombination of electrons following injection into the semiconductor:



Two possibilities of recombination exist: either with the oxidised dye or with the oxidized redox mediator.

The above reactions can be suppressed by the purposeful addition of hydrophobic groups to the dye hindering electron back from  $\text{TiO}_2$ .

(c2) Recombination reactions of electrons from the mesoporous semiconductor conducting support, usually TCO glass.



An effective way to suppress the above reactions is the juxtaposition of a thin compact oxide layer, termed underlayer, blocking layer or buffer layer, between the porous semiconductor and the support. Since the above reactions are particularly deleterious for one-electron fast redox mediators or solid-state hole conductors, developing an effective underlayer is essential. Typical methods for preparing underlayers are atomic layer deposition, spray pyrolysis, electrochemical deposition or screen printing. For the iodide-triiodide system, where the two electron reduction is rather sluggish in the absence of electrocatalyst, adding an underlayer may be less essential.

### 3.3 Mass Transport

Proper consideration should be paid to the mass transport of the redox mediator between the working electrode and the counter electrode. For several inorganic coordination complexes of large

size  $r$  the diffusion coefficient  $D$  would be not favourable for efficient DSSC performance, especially if the viscosity of the electrolyte  $\eta$  is elevated.  $D$ ,  $r$  and  $\eta$  are approximately related by the Stokes-Einstein Eqn.:<sup>[87]</sup>

$$D = RT/N_A 6\pi\eta r \quad (17)$$

where  $R$  and  $T$  are the universal gas constant and the absolute temperature, respectively. The applicability of the above equation is better at low concentrations of the mediator. In fact,  $D$  depends on the concentration, expected to decrease with increased concentration. However, in some cases an increase of the apparent diffusion coefficient with concentration can be observed due to the beneficial effect of electron or atom hopping. The former can occur for inorganic coordination-type mediators, the latter is possible for the  $I^-/I_3^-$  redox system. The apparent diffusion coefficient  $D_{\text{app}}$  is related to the physical (low-concentration) diffusion coefficient  $D$  by the Dahms-Ruf Eqn.:<sup>[88,89]</sup>

$$D_{\text{app}} = D + k_{\text{ex}} [M^+][M^0]\delta^2/6 \quad (18)$$

where  $k_{\text{ex}}$  is a second-rate constant,  $[M^+]$  and  $[M^0]$  are the concentration of the reduced and oxidized state, and  $\delta$  is the distance between  $M^+$  and  $M^0$ .

In the case of the copper-based coordination redox mediators discussed in Section 4.2,  $D$  has a value between 1 and  $4 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$  in acetonitrile,<sup>[90]</sup> of the same order of magnitude as for  $I^-$  and  $I_3^-$  ( $2 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ <sup>[91]</sup>).  $D$  for Co mediators, is notably lower, between 5 and  $9 \times 10^{-6}$ .<sup>[92]</sup> Due to the slow diffusion of redox mediators, low-viscosity but volatile acetonitrilic electrolytes are preferred in fundamental DSSC research.

Until around 2010 DSSC research and development was based on the iodide redox mediator and considerable efforts were devoted to the development and optimization of low-volatility electrolytes based either on molecular solvents or room-temperature organic molten salts, commonly designated as ionic liquids. From 2010, an increased emphasis has been paid to alternative redox mediators, mainly metal coordination complexes, and to a lesser extent organic metal-free species. Each mediator needs its own electrolyte development. Such efforts are seriously hampered by the slow diffusion of the new mediators, although the possibility of electron hopping assisting molecular diffusion should be exploited. Therefore, the main emphasis has been the optimization of mediators and suitable dyes, while keeping the most diffusion-favourable option of acetonitrilic electrolytes. It can be argued that giving priority to demonstrating the possibility of DSSC efficiency exceeding 15% in acetonitrile electrolytes could encourage substantial research in the development of alternative more stable electrolytes or solid-state media.

The counter argument is that electrolyte development takes a long time, as evident from development of other types of electrochemical energy devices, and, in any case, a solar cell as efficient as solid-state cells but based on a volatile electrolyte will not be applicable despite the high efficiency. Therefore, simultaneous efforts should be devoted to both optimizing the DSSC efficiency with volatile electrolytes and optimizing the electrolyte with solar cells exhibiting the best performance achievable with the actual state-of-the-art. That said, the individual preferences of researchers involved in DSSC research are bound to play an important role in the particular direction where rapid progress may be achieved.

### 3.4 Counter Electrodes

For each redox mediator the performance of the counter electrode catalyst should be properly evaluated. Platinum, a catalyst of choice for iodide-triiodide, reviewed by Papageorgiou,<sup>[93]</sup> may

not be the best choice for other redox mediators. The electrode kinetics of Cu coordination redox mediator complexes, like the kinetics at several other redox mediators, at the counter electrode (CE) requires an electrocatalyst. The properties of counter electrodes have been reviewed by Theertagiri *et al.*<sup>[94]</sup> and by Ma *et al.*<sup>[95]</sup> as well as in the monograph edited by Yun and Hagfeldt.<sup>[96]</sup> For inorganic coordination-type redox mediators, an efficient electrocatalytic material is the electronically conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). For this material a facile preparation method is the electrochemical deposition on FTO glass from an aqueous micellar solution of the EDOT monomer;<sup>[97]</sup> in the case of Cu and Co coordinated redox mediator this catalyst often behaves better than thin-layer platinum.

#### 4. Solar Cell Device Performance

Here a selected number of systems corresponding to relatively high solar energy conversion efficiency is reported, together with some milestone cases pointing out to the possibility of replacing the iodide redox mediator, a relatively complex, two-electron system, with simpler one-electron mediators. A comprehensive review covering the use of inorganic coordination complexes in DSSCs has recently been published by Saygili *et al.*<sup>[98]</sup>

As regards scientific terminology, an often occurring confusion between the terms mediator and electrolyte should be pointed out. Mediator is the molecular system transporting charge between photoelectrode and counter electrode. Electrolyte is an ionic conductor, which may contain redox-active species or not. Occasionally in chemistry the term electrolyte designates species which dissociate into ions upon dissolution in a solvent. Hence a charged solid coordination complex with its counterions can be called an electrolyte in this sense.

However, some redox mediators are uncharged in the reduced state, oxidised state, or both. A typical example is the redox mediator system hydroquinone-benzoquinone, both of which are electrically neutral. Therefore, the term electrolyte should never be used for the mediator itself. Occasionally the term redox electrolyte is encountered. The use of this term for electrolytes containing redox mediators is not recommended by the present authors, with one possible exception: ionic liquids with cation, anion or both being redox active species. Example: ionic liquids with iodide anion or cation with a ferrocene pendant group. Such electrolytes, with sufficiently low viscosity, may be interesting as charge-transport media for DSSCs in the future.

#### 4.1 Iodide and Cobalt-based Redox Mediators

The highest efficiency (certified) for I<sup>-</sup>/I<sub>3</sub><sup>-</sup>-based DSSCs is 11.9% under full sun according to Komiyama *et al.*<sup>[99]</sup> with an open-circuit voltage of 0.744 V. This is also the highest certified efficiency for a DSSC up-to-date. The I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox mediator has several advantages, including low cost, high solubility, fast diffusion, relatively low electrochemical overpotential for several counter electrode catalysts, and slow recombination at the conducting glass substrate. A key disadvantage is the substantial Gibbs energy required for dye regeneration, as high as 0.5eV, thereby posing a serious limitation to the cell performance. This is due to the fact that several coupled electrochemical and chemical steps are required for the overall two-electron reaction of iodide oxidation to triiodide. Therefore, alternative redox mediators have been of considerable interest since the earlier days of DSSC development.

The first efficient alternative mediator option has been provided by cobalt coordination complexes after the promising initial results by Hagfeldt and collaborators,<sup>[92]</sup> based on cobalt tris-bipyridine in conjunction with an organic dye containing appropriate pendant groups. These groups are essential toward blocking electron recombination at the TiO<sub>2</sub>/electrolyte inter-

face. This result initiated further investigation, and soon thereafter cobalt-based systems surpassed in efficiency these with iodide-based electrolytes. The actual performance record of 14% full-sun efficiency, with an open-circuit voltage of 1V, has been achieved by Kakiage *et al.*<sup>[4]</sup> by coupling a cobalt electrolyte to a photoelectrode coated with two organic, metal-free sensitizers.

#### 4.2 Copper-based Redox Mediators

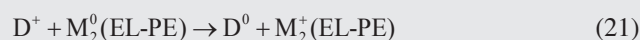
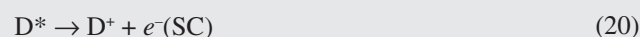
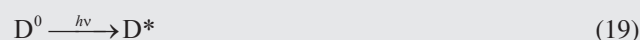
Copper complexes have the advantage, in comparison to cobalt complexes, of lower cost, and faster diffusion. Their first use in DSSCs based on a ruthenium sensitizer was reported by Hattori *et al.*<sup>[100]</sup> In the last decade Cu mediators, with phenanthroline or bipyridine-based ligands, in DSSCs with organic metal-free dyes, have been extensively investigated in the laboratories of Anders Hagfeldt (Sweden and Switzerland), Gerrit Boschloo, Marina Freitag, Licheng Sun and Lars Kloo (Sweden), and Michael Grätzel (Lausanne), with efficiency comparable to that achieved with cobalt complexes and the additional advantage of higher photovoltage.<sup>[18,90,101–103]</sup> The highest efficiency of 13.1% at full sun has been obtained by Cao *et al.*<sup>[103]</sup> with an open-circuit photovoltage of 1.1 V. The photoelectrode was coated with two organic metal-free sensitizers. The improved efficiency, compared to the previously reported values of 10%<sup>[101,103]</sup> was due to the fact that the photoelectrode was pressed against the PEDOT-based counter electrode so that the interelectrode gap was minimal and the mass-transport of the mediator optimized. Additionally, DSSCs with Cu redox mediators have been demonstrated to be highly efficient when exposed to indoor 1000 Lux irradiance according to Freitag *et al.*<sup>[104]</sup> with an efficiency of 32% and open-circuit photovoltage of 0.82V. Their performance was superior to that of solid-state GaAs cells deposited on a flexible substrate (21% efficiency with 0.94V photovoltage).

#### 4.3 Co-mediators

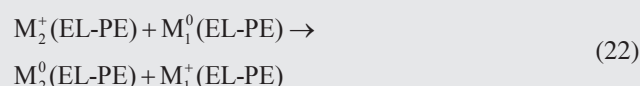
An alternative approach is that of dual mediators. Redox species M<sub>1</sub><sup>+</sup>/M<sub>1</sub> is the mediator, responsible for charge transport between photoelectrode and counter electrode, and redox species M<sub>2</sub><sup>+</sup>/M<sub>2</sub>, or comediator, for dye regeneration. The system can be advantageous over that based on the mediator alone due to the faster regeneration by the chosen co-mediator, as well as that based on the co-mediator alone for various reasons, e.g. rapid recombination between oxidized dye and M<sub>2</sub><sup>+</sup>, strong light absorption by M<sub>2</sub><sup>+</sup>, slow diffusion M<sub>2</sub>/M<sub>2</sub><sup>+</sup>, or chemical instability of M<sub>2</sub><sup>+</sup> in the electrolyte. These reasons necessitate to keep the concentration of M<sub>2</sub><sup>+</sup> as low as possible. Usually amounts of M<sub>1</sub>, M<sub>1</sub><sup>+</sup> and M<sub>2</sub> are added and the concentration of M<sub>2</sub><sup>+</sup> is adjusted in the cell at a sufficient level to sustain stable DSSC operation.

The reaction sequence at the photoelectrode is presented below.

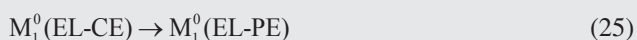
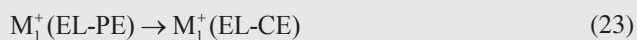
(a) Light absorption, injection, and regeneration:



(b) Reaction between oxidized comediator and reduced mediator at the proximity of the photoelectrode:



(c) Diffusion of the oxidized mediator to the counter electrode, electroreduction, and back diffusion of the reduced mediator to the photoelectrode:



An efficient co-mediator system has been described by Hao *et al.*,<sup>[105]</sup> with a cobalt complex as mediator and p-anisylamine (TPAA) as co-mediator, with an  $\eta_{\text{EFF}}$  of 10.5% at full sun and an open-circuit voltage of 0.92V.

### 5. 'Zombie Cells'

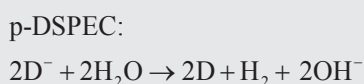
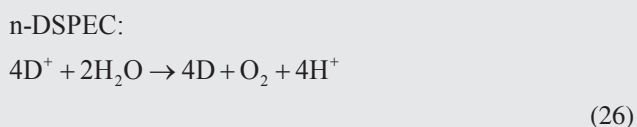
An important alternative variety of the DSSC with a liquid electrolyte containing a copper coordination complex is generated by evaporation of the acetonitrile solvent so that a solid-state hole conductor based on the same complex is generated. The discovery of this cell is due to pure serendipity. Some used dry DSSCs were measured in Sweden with the purpose of testing the functioning of a DSSC measuring instrumentation setup under development, and, quite surprisingly, it was demonstrated that the spent cells were more efficient than either the same cells in the past, immediately after assembly, or similarly prepared fresh cells. This is the origin of the colloquial name 'Zombie cell' – abbreviated to Z-cell – in fact cells thought as dead cells resuscitated. According to Freitag *et al.*,<sup>[106]</sup> a copper mediator cell exhibited an efficiency of 8.2% as Z-cell (open-circuit photovoltage of 1.01 V) under full sun as compared to 6.0% and 1.04 V for a liquid cell prepared by the same method at the same time. Improved performance for Z-cells has been reported by Cao *et al.*,<sup>[107]</sup> with 11.0% efficiency under full sun (open-circuit photovoltage of 1.08 V). It was established that the cell should contain the solidified hole conductor in the amorphous state in preference to the crystalline state. The long-term stability was noteworthy, with a less than 15% loss of the initial efficiency under prolonged irradiation under 50% sun for 200 hours.

### 6. Basic Principles of Operation of Fuel-generating Dye Solar Cells

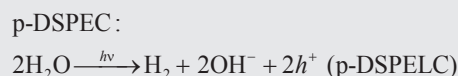
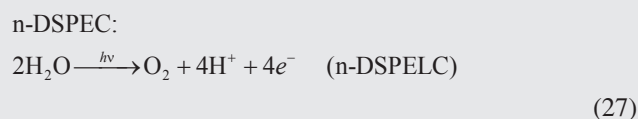
In a dye-sensitized photoelectrolysis cell (DSPECs) different reactions take place at the PE and the CE, resulting in a net endoergic chemical change in the solution. Several reviews discussed the general features of DSPECs and the underlying physicochemical principles.<sup>[25–34,37,48,59,70,72–75]</sup> The emphasis in this section will be water splitting to hydrogen and oxygen, but some other approaches will be briefly mentioned.

The description of irradiated dye-sensitized p-type semiconductor electrodes is analogous to that of n-type semiconductor electrodes. Upon irradiation, the excited state  $D^*$  is converted to  $D^-$  by injecting a hole into the semiconductor valence band (or, equivalently, by capturing an electron from the valence band).

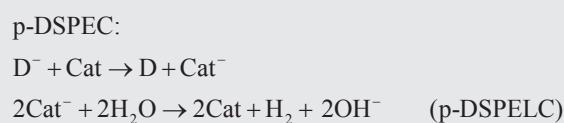
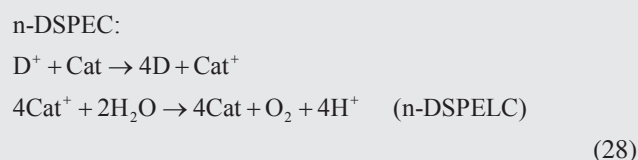
If the overall reaction is the splitting of water to hydrogen and oxygen, the overall dye regeneration reaction in a neutral solution is



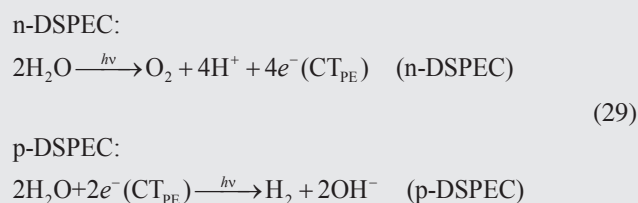
and the overall PE reaction is



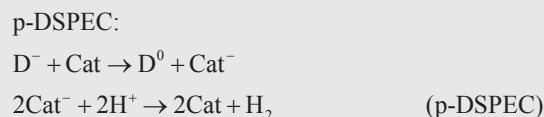
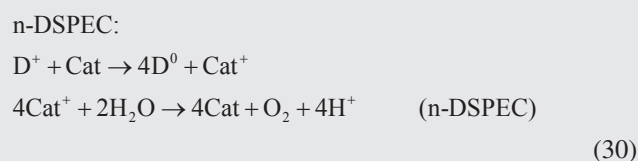
The dye regeneration linked to oxygen evolution at a n-PE or hydrogen evolution at a p-PE involves a complex reaction, usually necessitating the addition of a catalyst. For example, heterogeneous micro-dispersed catalysts or molecular redox catalysts have been used in DSPEC systems. In the latter case, the reaction sequence can be formulated so as to include two steps, the regeneration of the dye by oxidation or reduction of the catalyst, followed by the regeneration of the catalyst in a series of reactions with water or its components:



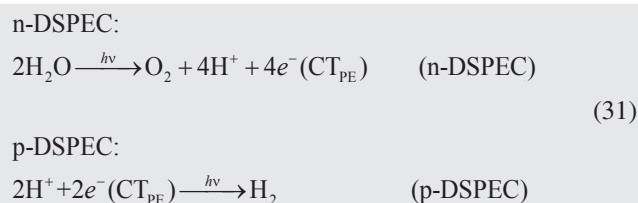
The overall reaction at the PE in a neutral solution is



Usually DSPECs involve reactions in neutral, moderately acidic or moderately basic solutions, and basic solutions. In the case of strong acidic solutions, the above equations have to be partially reformulated. For acidic solutions the reactions involve  $H^+$  and  $H_2O$ . The dye regeneration is

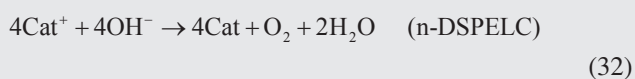
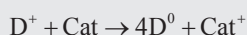


and the overall PE reaction

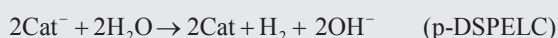


For alkaline solutions the reactions involve  $\text{H}_2\text{O}$  and  $\text{OH}^-$ . The dye regeneration is

n-DSPEC:

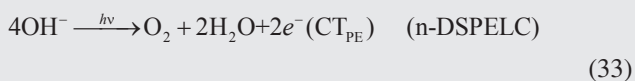


p-DSPEC:

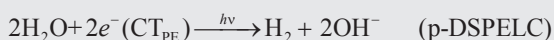


and the overall PE reaction

n-DSPEC:



p-DSPEC:



Three basic types of DSPECs can be envisaged; with n-PE and dark CE, with p-PE and dark CE, and with both n-PE and p-PE. The first two types of cell may require an external bias potential ( $U_{\text{bias}}$ ) if the energy available at the PE is not sufficient to drive the overall reaction. The third type can operate at short-circuit.

### 6.1 n-Type DSPECs

In an n-type PEC, depicted in Fig. 4, the mechanism of the dye regeneration reaction with water toward oxygen evolution is quite complex. One of the two half reactions, the oxidation of water to  $\text{O}_2$  (oxygen evolution reaction, OER), necessitates an injection of four holes from the oxidized dye, and is expected to involve several electron transfer and intermediate steps. Therefore, the value of the free-energy change should be quite large, and the involvement of a catalyst is often required. In this respect, two broad groups of OER catalysts have been considered, molecular OECs and heterogeneous microdispersed OECs.

For molecular OECs, there has been a synergy between research in DSPECs and in molecular catalysis. Typical tests of suitable catalysts involve their application to the acceleration of the exoergic oxidation reaction of water by the strong oxidant  $\text{Ce}^{4+}$ . Several effective catalysts incorporate Ru (Ru-OEC), as suggested, for example, in several studies of the research groups and associated collaborators of L. Sun,<sup>[35,36,38,39–45]</sup> Y. Gao,<sup>[46]</sup> and T. J. Meyer.<sup>[47,49,50]</sup> In Fig. 5 the structure of a Ru-based dye and Ru-based water oxidation catalyst applied in DSPEC are shown.

As regards the energetics at the PE, the lowest unoccupied molecular orbital (LUMO) of the dye has to lie above the  $\text{TiO}_2$  conduction band for efficient electron injection, the latter approximately equal to 0.1 eV<sub>/RHE</sub> (i.e. vs. the Fermi level of electrons equilibrating with the reversible hydrogen electrode). The HOMO of the dye should lie, on account of the complex kinetics of  $\text{O}_2$  evolution, significantly below the Fermi level of  $\text{O}_2/\text{H}_2\text{O}$  equal to 1.23 eV<sub>/RHE</sub>. Therefore, dyes with LUMO-HOMO gap substantially larger than these encountered in electricity-generating DSSCs are needed, thereby limiting the light harvesting efficiency and, as a result, the overall energy storage efficiency.

Several of such studies are based on sensitization by a ruthenium tris(bipyridine) ( $\text{Ru}(\text{bpy})_3$ )-based dye equipped with phosphonate groups for effective surface attachment. It is preferable that the catalyst is immobilized at the electrode. This can be achieved by several approaches, of which the most used are the co-adsorp-

tion with the dye<sup>[36,38,39,42,44]</sup> and the supramolecular covalent attachment to the dye.<sup>[45,47,49,50]</sup> Alternative methods are: the inclusion into a Nafion<sup>®</sup> layer superimposed to the electrode,<sup>[40]</sup> linkage to the dye by a  $\text{Zr}^{4+}$  bridge,<sup>[35]</sup> and formation of a host-guest complex of cyclodextrin.<sup>[43]</sup>

Transient current vs. time photocurrents for the mediated  $\text{O}_2$  evolution exceeding 1 mAcm<sup>-2</sup> were obtained in aqueous solutions with pH in the range 4–7 by Alibabaei *et al.* (monochromatic 445 nm light, 86 mWcm<sup>-2</sup>),<sup>[47]</sup> Li *et al.* (light from Xe lamp, 300 mWcm<sup>-2</sup>),<sup>[41,43]</sup> and Zhang *et al.*<sup>[46]</sup> (illumination as before). All of these studies were based on sensitization by a phosphonated  $\text{Ru}(\text{bpy})_3$  dye (Fig. 5) with a favourable  $\text{D}^+/\text{D}$  redox potential toward  $\text{O}_2$  evolution in weak acidic or neutral media. The fact that the photocurrent declines with time points to the fact that the regeneration of the oxidized dye by the mediator does not compete favourably with the various recombination mechanisms of the injected electrons either with the oxidized dye, the oxidized catalyst, oxygen or various intermediates of the OER.<sup>[43]</sup> In several other publications on DSPEC studies mentioned in this review the photocurrent densities reported are below 1 mAcm<sup>-2</sup>, indicating that the solar energy storage efficiency is inferior to 1%. Apart from the Ru-based dye mentioned above, other dyes can be used for DSPEC oxygen-evolving systems mediated by redox catalysts. The dye used by Yamamoto *et al.*<sup>[44]</sup> was a push-pull type boron-centred sub porphyrin, with  $-\text{COOH}$  attachment groups. In the study by Yamamoto *et al.*<sup>[45]</sup> the dye was a Zn-centred porphyrin with  $-\text{COOH}$  attachment groups. In the tandem n-p-DSPEC proposed by Li *et al.*<sup>[40]</sup> the sensitizer at the n-PE was an organic metal-free charge-transfer dye.

In several of their studies, Meyer and collaborators used a core-shell structure for the dye-absorbing PE.<sup>[47–49,51]</sup> The lat-

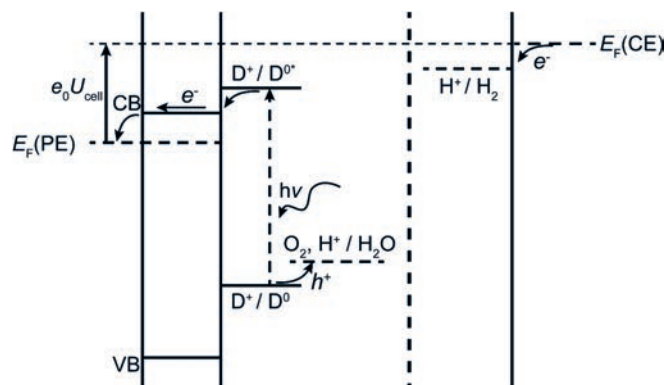


Fig. 4. Energy diagram for a dye-sensitized photoelectrosynthetic cell with an n-type anodic PE and a dark cathodic CE.

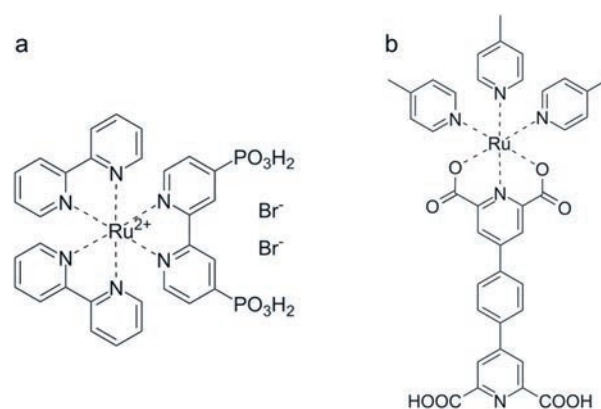


Fig. 5. Examples of dye (a) and oxygen evolution catalyst (b) of dye-sensitized photoelectrosynthetic cells. Reprinted by permission from www.dyenamo.se. Copyright 2017 Dyenamo.

ter is composed of SnO<sub>2</sub> particles (core) surrounded by a very thin TiO<sub>2</sub> layer active in dye absorption. The advantage is that the conduction band of SnO<sub>2</sub> lies lower than that of TiO<sub>2</sub> so that electron recombination is hindered, with the electrons originating from the PE contact having to surmount a barrier equal to  $E_{CB}(\text{TiO}_2) - E_{CB}(\text{SnO}_2)$ . In addition, since the range of values between  $E_{CB}(\text{SnO}_2)$  and  $E_{CB}(\text{TiO}_2)$  is not accessible to  $E_F(\text{SnO}_2)$ , the electron recombination can be kept at a lower rate for the core-shell material than in the case of the usual TiO<sub>2</sub> substrate. The drawback is that the difference,  $E_{CB}(\text{H}_2) - E_{CB}(\text{PE})$ , which electrons flowing to the external circuit have to be overcome is larger for the core-shell PE. In brief, the kinetic advantage is counterbalanced by a thermodynamic loss. The TiO<sub>2</sub> shell is generated by the atomic-layer deposition method (ALD).

As regards OER catalysts, species not containing Ru or combining a Ru species with a species without Ru have been tested; however, the systems incorporating such catalysts have proven so far less efficient than some of the ones previously described, with the photocurrents obtained being inferior to 1 mAcm<sup>-2</sup>. In this respect tetranuclear Mn cubane cluster complexes [Mn<sub>4</sub>O<sub>4</sub>]<sup>6+</sup>, of a structure similar to that encountered in the natural photosynthesis system, immobilized into a Nafion<sup>®</sup> ion-exchange polymer layer, have been the subject of investigations of the groups of Dismukes, Spiccia, and their collaborators.<sup>[52,53,70]</sup> In these studies, the PE was sensitized with a Ru tris(bipyridine)-type dye with -COOH attachment groups. The polyoxometallate OER catalyst [ $\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})\}^{10-}$ ] at a PE sensitized by a phosphonated Ru(bpy)<sub>3</sub>-type was reported by Xiang *et al.*<sup>[54]</sup> An Ir-cyclopentenediyl-type complex was the OER in a study by Moore *et al.*<sup>[55]</sup>

As far as heterogeneous catalysts are concerned, the use of colloidal IrO<sub>2</sub> has been proposed by Mallouk and co-workers,<sup>[30,33]</sup> with the catalyst particles covalently attached to the phosphonated Ru(bpy)<sub>3</sub> sensitizing dye.

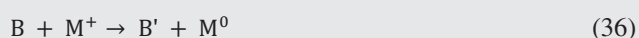
In addition to oxygen evolution, other oxidation reactions can be envisaged, in particular those that generate useful products. Treadway *et al.*<sup>[108]</sup> reported a DSPEC with Ru-based sensitizer which effects the oxidation of 2-propanol, which is the solvent in the photoelectrode electrolyte to acetone



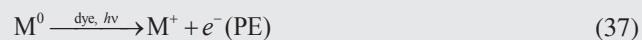
with a redox potential of 0.64V vs. SHE, substantially less positive than that of water oxidation to oxygen. This reaction is of possible practical interest, since it is a part of one of the industrial processes of acetone production, based on the hydration of propene to propanol followed by the above reaction. If the CE half-reaction is the hydrogen evolution, the overall reaction is



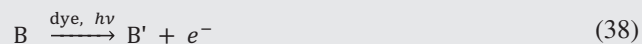
The PECs discussed up to now were photoelectrosynthetic cells, in which an overall uphill reaction is performed. However, photocatalytic cells, in which the overall reaction is downhill, may be of interest since the reactants are inexpensive, eventually available in industrial or municipal effluents. An interesting option which has attracted some attention is that of the dye-sensitized biofuel or bioelectrolysis cell, systematically investigated by Thomas A. Moore and co-workers.<sup>[109,110]</sup> The basic reaction is the spontaneous oxidation of a fuel (B) in presence of an oxidized redox mediator M<sup>+</sup>, resulting in the generation of decomposition products (B') and, simultaneously, the reduction of the mediator



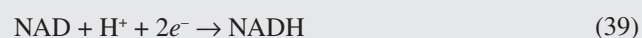
M is regenerated at the photoelectrode, according to the mechanisms described before:



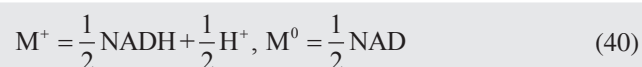
so that the overall reaction at the PE would be



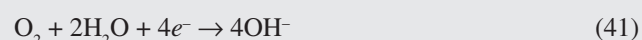
In the publications mentioned above the substrate was glucose and the mediator system was the well known biological metabolite nicotinamide adenine dinucleotide NADH<sup>+</sup>/NAD



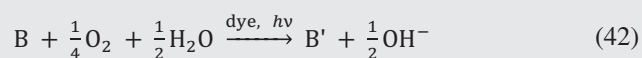
with



Two possibilities exist for the coupled CE reaction. One is the reduction of O<sub>2</sub>:



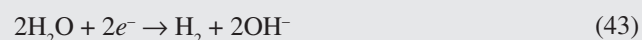
with simultaneous generation of electricity, so that the system works in the biofuel cell mode, generating electricity by the decomposition of the substrate:



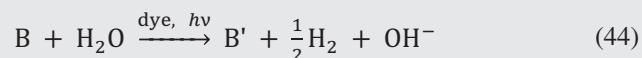
where, since biofuel cells mostly operate at near-neutral pH, the H source is water rather than H<sup>+</sup>.

This system, upon further development, would be of interest as an alternative to the current DSSC if the cell components are less expensive than these of the current DSSCs and if, in place of glucose, species originating from effluents are used, so that electricity would be generated together with effluent remediation.

The other possibility is the H<sub>2</sub> evolution at a short-circuited PE:



so that the overall reaction is



so that such a system, upon further development, would effect the generation of H<sub>2</sub> together with effluent remediation.

## 6.2 p-Type and Tandem n-p-Type DSPECs

For the reaction at a p-DSPEC, depicted in Fig. 6, the operation resembles in several aspects that of a n-DSPEC, with the excited state injecting holes into the valence band (VB) of the oxide support and the photoreduced dye being regenerated by injecting an electron to the oxidized form of a redox species.<sup>[34]</sup> The two-electron reduction reaction of water to hydrogen is a complex reaction, involving several steps, like the more com-



plex oxygen evolution reaction. Therefore, a hydrogen evolution catalyst (HEC), molecular redox or heterogeneous, may be needed. Up to the present time, the photocurrents observed for p-DSPECs under simulated full sun has been inferior to  $1 \text{ mAcm}^{-2}$ .

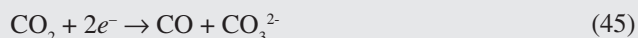
The preferred semiconductor as a substrate is mesoporous p-NiO, which has been initially used in electricity-generating p-DSSCs as well as in two-PE n-p-DSSCs.<sup>[56]</sup> Physicochemical aspects of NiO related to photoelectrosynthetic systems have been described by Gibson, Tian, and Wood *et al.*<sup>[31,57,72]</sup> In several studies the HER redox catalyst is the cobalt coordination complex  $\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2$  (commonly called cobalamine or cobaloxime), where  $\text{dmgBF}_2^-$  is the difluoroboryldimethylglyoximate anion; a variant of this catalyst, chemically modified by attachment of a carboxylated N-N bipyridine group so as to allow covalent attachment to  $\text{TiO}_2$  (see below).

In general, organic metal-free dyes have been preferred as sensitizers for NiO, as in the cases reported in this section, unless otherwise specified. The electrolyte was aqueous, with pH between 5 and 8, unless otherwise indicated.

In the earlier study of Li *et al.*<sup>[58]</sup> the cobalamine catalyst was been used in the dissolved state; in that case the electrolyte was 1:1 water-acetonitrile at pH 7. In the studies by Ji *et al.*,<sup>[60]</sup> Kaeffer *et al.*,<sup>[61]</sup> and Pati *et al.*,<sup>[62]</sup> the same catalyst was covalently attached to the dye; for Ji *et al.* the sensitizer was a Ru coordination complex. In the dye-sensitized p-cathode of the tandem n-p cells studied by Fan *et al.*,<sup>[63]</sup> and Li *et al.*,<sup>[42]</sup> the same catalyst, appropriately modified, was co-adsorbed together with the dye on  $\text{TiO}_2$ . Heterogeneous HECs were used by Hoogeveen *et al.*,<sup>[64]</sup> where the catalyst was microparticulate Pt deposited on the NiO electrode, and by Click *et al.*,<sup>[65]</sup> where the catalyst was the molybdenum sulphide cluster  $[\text{Mo}_3\text{S}_4]^{4+}$  dissolved into the electrolyte. Exceptionally for DSSPEC studies, the electrolyte in the study of Click *et al.* was acidic, 0.1M  $\text{H}_2\text{SO}_4$ , so as to ensure good solubility and stability of the catalyst. In this case the highest stable photocurrent, exceeding  $100 \mu\text{Acm}^{-2}$ , so far reported for hydrogen evolution at dye-sensitized NiO, was obtained under white light illumination (Xe lamp,  $344 \text{ mWcm}^{-2}$ ). Fig. 7 shows an organic metal-free dye and a cobalt catalyst for hydrogen evolution catalyst at NiO.

As regards to tandem DSPECs, as depicted in Fig. 8, the lower efficiency of the p-type PE will play a determining role to the overall performance of the system, with stable photocurrents below  $100 \text{ mA/cm}^2$  under irradiation with simulated sunlight. Fan *et al.*<sup>[25]</sup> and Li *et al.*<sup>[42]</sup> demonstrated the possibility of water decomposition in a neutral electrolyte without external bias potential. In both studies the sensitizer at the p-PE was an organic metal-free dye. Fan *et al.* used the aforementioned phosphonated  $\text{Ru}(\text{bpy})_3$ -type dye as n-PE sensitizer; contrarily, in the study Li *et al.* the n-PE sensitizer was an organic metal-free dye.

Apart from the  $\text{H}_2$  evolution reaction, the  $\text{CO}_2$  reduction at DSPECs has attracted some attention.<sup>[111–113]</sup> Apart from the possibility of the generation of useful chemicals, its successful implementation would contribute to a diminishment of the  $\text{CO}_2$  amount in the atmosphere. However, this is an uphill reaction, requiring the disruption and creation of several chemical bonds. One of the simple reactions, not requiring a proton source, is the generation of CO, with carbonate as by-product:



This reaction is observed in both aqueous and nonaqueous solvents. In aqueous or mixed aqueous-nonaqueous solvents a serious disadvantage is the simultaneous  $\text{H}_2$  evolution. Therefore, the design of catalysts mediating  $\text{CO}_2$  in favour of + or  $\text{H}_2\text{O}$  reduction is essential. However, more useful products, *e.g.* alcohols, ethyl-

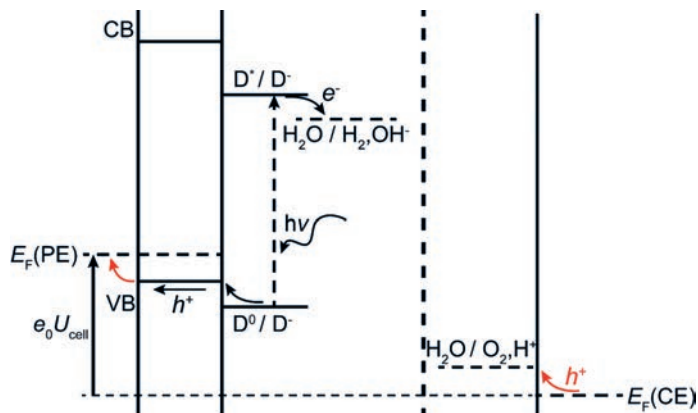


Fig. 6. Energy diagram for a dye-sensitized photoelectrosynthetic cell with a p-type cathodic PE and a dark anodic CE.

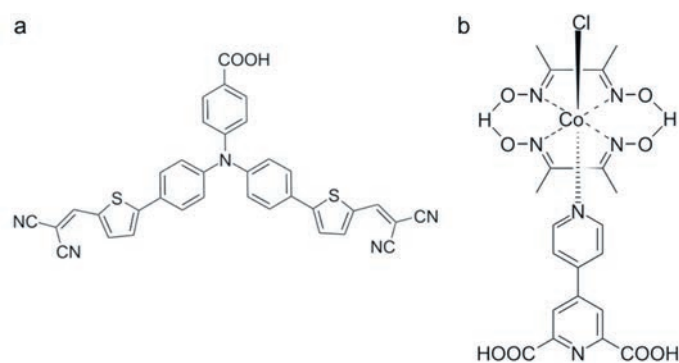


Fig. 7. Examples of dye (a) and hydrogen evolution catalyst (b) of dye-sensitized photoelectrosynthetic cells. Reprinted by permission from [www.dyenamo.se](http://www.dyenamo.se). Copyright 2017 Dyenamo.

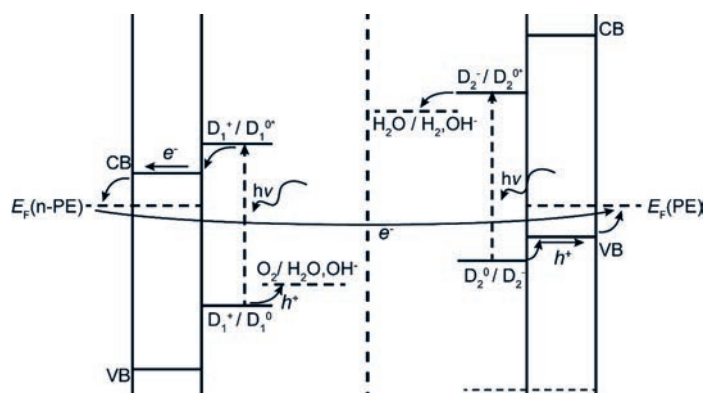


Fig. 8. Tandem n-p dye-sensitized photoelectrosynthetic cell for water splitting operating at short-circuit, without simultaneous electricity generation. The long red-coloured arrow indicates transport of electrons from n-PE to p-PE.

ene, methane, can be generated in presence of water, or another protic source, the amount of which in a mixed solvent would depend on the catalyst choice.

## 7. Future Outlook

Although the general principles of the operation of dye-sensitized solar cells (DSSCs) and dye-sensitized photoelectrochemical cells DSPECs, generating electricity and chemicals from sunlight, respectively, are well understood, as explained in the present review, the details of several mechanisms are far from being fully elucidated. On the one hand the physics and chemistry of nanostructured semiconductors poses several challenges to theoretical and experimental scientists alike. Several concepts from traditional solid-state physics based on well-defined crys-

talline materials cannot be directly applied to the type of porous semiconductors encountered in dye-based devices. Secondly, new molecular compounds are continuously introduced, and their properties have to be studied at the same time as their application to DSSCs or DPECs.

With respect to DSSCs, the goal of DSSC future research is the achievement of an efficiency surpassing 15% simultaneously with enhanced long-term stability and low cost. Therefore, an important goal is the synthesis of sensitizers absorbing more into the infrared part of the solar spectrum. At the same time, the need to develop stable non-volatile liquid or solid charge-transfer media should not be disregarded. With respect to cost reduction, sensitizers, redox mediators and counter-electrode substrates without noble or other expensive metal substrates should be preferred.

An important advantage of the DSSCs is the larger open-circuit photovoltage compared to silicon and some other solid-state DSSCs, under both full sun and diffuse or indoor illumination. In this respect, the continuation of past research efforts is needed with respect to identifying stable dye-redox mediator systems with low driving force for dye regeneration together will effective blocking of the dark recombination reactions.

As regards to the application of dye-sensitized photoelectrolysis cells (DSPECs) to the generation of fuels or other useful chemicals, progress has been slower, despite the important scientific insights attained by studies of such systems. The energy levels of the dye-semiconductor interface have to be matched with these of two, not one, redox systems, and this limits the choice of suitable dyes. In particular, identifying dyes with a HOMO lower than that of the energy levels involved in the oxygen/water system and, at the same time, with a LUMO above that of the semiconductor band edge, is an uphill challenge. Moreover, the higher HOMO-LUMO gap for such dyes will render them inferior light harvesters compared to the dyes actually targeted for DSSC applications. An additional challenge is the more complex electron transfer mechanisms for dye regeneration in solar fuel; reactions, requiring sophisticated catalyst systems. The most interesting solar fuel systems are based in water so that the design of stable hydrophobic dyes is a further requirement.

All in all, the DSPEC design requires a development radically different than that for DSSCs. Therefore, the achievement of energy conversion efficiencies compared to those of actual DSSCs should be perceived as a medium-to-long perspective goal. However, that said, compared to photoelectrochemical systems based on semiconductor light absorbers, a larger flexibility is expected for DSPEC-compatible molecular systems, with practically limitless variants to be tested and optimized. It is hoped that the fascinating scientific perspective related to the DSPEC field, provided that the availability appropriate research funding for this purpose is guaranteed, will lead in step with the further enhancement of the necessary scientific background, to the gradual improvement of the performance of PEC systems.

### Acknowledgement

Anders Hagfeldt acknowledges financial support from the Swiss National Research Foundation, grant number 200020-185041. The authors thank Dr Linfeng Pan for designing the figures of the photoelectrochemical cells.

- [1] E. A. Gibson, A. Hagfeldt, in 'Energy Materials', Eds. D. W. Bruce, D. O'Hare, R. I. Walton, **2011**, pp. 95, DOI: 10.1002/9780470977798.ch3.
- [2] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-I. J. Fujisawa, M. Hanaya, *Chem. Commun.* **2015**, 51, 15894, DOI: 10.1039/C5CC06759F.
- [3] M. A. Green, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger, M. Yoshita, A. W. Y. Ho-Baillie, *Prog. Photovoltaics Res. Appl.* **2019**, 27, 565, DOI: 10.1002/pip.3171.
- [4] S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, *J. Am. Chem. Soc.* **2010**, 132, 16714, DOI: 10.1021/ja1088869.
- [5] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, 95, 49, DOI: 10.1021/cr00033a003.
- [6] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **2000**, 33, 269, DOI: 10.1021/ar980112j.
- [7] M. Grätzel, *Nature* **2001**, 414, 338, DOI: 10.1038/35104607.
- [8] J. Bisquert, D. Cahen, G. Hodes, S. Rühle, A. Zaban, *J. Phys. Chem. B* **2004**, 108, 8106, DOI: 10.1021/jp0359283.
- [9] M. Grätzel, *Inorg. Chem.* **2005**, 44, 6841, DOI: 10.1021/ic0508371.
- [10] L. Peter, in 'ECS Transactions', Vol. 6, ECS, **2007**, pp. 555, DOI: 10.1149/1.2731224.
- [11] L. M. L. M. Peter, *Phys. Chem. Chem. Phys.* **2007**, 9, 2630, DOI: 10.1039/b617073k.
- [12] S. Ardo, G. J. Meyer, *Chem. Soc. Rev.* **2009**, 38, 115, DOI: 10.1039/b804321n.
- [13] M. Grätzel, *Acc. Chem. Res.* **2009**, 42, 1788, DOI: 10.1021/ar900141y.
- [14] B. C. O'Regan, J. R. Durrant, *Acc. Chem. Res.* **2009**, 42, 1799, DOI: 10.1021/ar900145z.
- [15] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, 110, 6595, DOI: 10.1021/cr900356p.
- [16] 'Dye-sensitized solar cells', Ed. K. Kalyanasundaram, EPFL Press, Lausanne, **1990**.
- [17] G. J. Meyer, *ACS Nano* **2010**, 4, 4337, DOI: 10.1021/nn101591h.
- [18] M. Freitag, G. Boschloo, *Curr. Opin. Electrochem.* **2017**, 2, 111, DOI: 10.1016/j.coelec.2017.03.011.
- [19] I. Benesperi, H. Michaels, M. Freitag, *J. Mater. Chem. C* **2018**, 6, 11903, DOI: 10.1039/C8TC03542C.
- [20] N. Vlachopoulos, J. Zhang, A. Hagfeldt, *Chimia* **2015**, 69, 41, DOI: 10.2533/chimia.2015.41.
- [21] A. Fujishima, K. Honda, *Bull. Chem. Soc. Jpn.* **1971**, 44, 1148, DOI: 10.1246/bcsj.44.1148.
- [22] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37, DOI: 10.1038/238037a0.
- [23] A. Fujishima, K. Kohayakawa, K. Honda, *Bull. Chem. Soc. Jpn.* **1975**, 48, 1041, DOI: 10.1246/bcsj.48.1041.
- [24] A. Fujishima, *J. Electrochem. Soc.* **1975**, 122, 1487, DOI: 10.1149/1.2134048.
- [25] Y. Zhao, J. R. J. Swierk, J. D. Megiatto Jr., B. Sherman, W. J. J. Youngblood, D. Qin, D. M. Lentz, A. L. Moore, T. A. Moore, D. Gust, T. E. Mallouk, J. D. Megiatto, B. Sherman, W. J. J. Youngblood, D. Qin, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 15612, DOI: 10.1073/pnas.1118339109.
- [26] J. j. Concepcion, R. L. House, J. M. Papanikolas, T. J. Meyer, T. J. Meyer, J. Concepcion, Javier J; Houser, Ralph L; Papanikolas, John M; Meyer, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 15560, DOI: 10.1073/pnas.1212254109.
- [27] M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, *Chem. Rev.* **2014**, 114, 11863, DOI: 10.1021/cr400572f.
- [28] A. Singh, L. Spiccia, *Coord. Chem. Rev.* **2013**, 257, 2607, DOI: 10.1016/j.ccr.2013.02.027.
- [29] W. Song, Z. Chen, M. Kyle Brennaman, J. J. Concepcion, A. O. T. Patrocinio, N. Y. Murakami Iha, T. J. Meyer, *Pure Appl. Chem.* **2011**, 83, 749, DOI: 10.1351/PAC-CON-10-11-09.
- [30] J. R. Swierk, T. E. Mallouk, *Chem. Soc. Rev.* **2013**, 42, 2357, DOI: 10.1039/c2cs35246j.
- [31] H. Tian, *ChemSusChem* **2015**, 8, 3746, DOI: 10.1002/cssc.201500983.
- [32] K. J. Young, L. A. Martini, R. L. Milot, R. C. Snoeberger, V. S. Batista, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.* **2012**, 256, 2503.
- [33] W. J. Youngblood, S.-H. A. Lee, K. Maeda, T. E. Mallouk, *Acc. Chem. Res.* **2009**, 42, 1966, DOI: 10.1021/ar9002398.
- [34] Z. Z. Yu, F. Li, L. Sun, F. Li, L. Sun, *Energy Environ. Sci.* **2015**, 8, 760, DOI: 10.1039/c4ee03565h.
- [35] X. Ding, Y. Gao, L. Zhang, Z. Z. Yu, J. Liu, L. Sun, *ACS Catal.* **2014**, 4, 2347, DOI: 10.1021/cs500518k.
- [36] K. Fan, F. S. Li, L. Wang, Q. Daniel, E. Gabrielsson, L. C. Sun, *Phys. Chem. Chem. Phys.* **2014**, 16, 25234, DOI: 10.1039/C4CP04489D.
- [37] J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* **2005**, 44, 6802, DOI: 10.1021/ic050904r.
- [38] Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li, L. Sun, *J. Am. Chem. Soc.* **2013**, 135, 4219, DOI: 10.1021/ja400402d.
- [39] Y. Gao, L. Zhang, L. Sun, **2014**, 2, 12008, DOI: 10.1039/c3cp55204g.
- [40] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, L. Sun, *Chem. Commun.* **2010**, 46, 7307, DOI: 10.1039/c0cc01828g.
- [41] F. Li, K. Fan, L. Wang, Q. Daniel, L. Duan, L. Sun, *ACS Catal.* **2015**, 5, 3786, DOI: 10.1021/cs502115f.
- [42] F. Li, K. K. Fan, B. Xu, E. Gabrielsson, Q. Daniel, L. Li, L. Sun, *J. Am. Chem. Soc.* **2015**, 137, 9153, DOI: 10.1021/jacs.5b04856.
- [43] H. Li, F. Li, Y. Wang, L. Bai, F. Yu, L. Sun, *Chempluschem* **2016**, 81, 1056, DOI: 10.1002/cplu.201500539.
- [44] M. Yamamoto, Y. Nishizawa, P. Chábera, F. Li, T. Pascher, V. Sundström, L. Sun, H. Imahori, *Chem. Commun.* **2016**, 52, 13702, DOI: 10.1039/c6cc07877j.
- [45] M. Yamamoto, L. Wang, F. Li, T. Fukushima, K. Tanaka, L. Sun, H. Imahori, *Chem. Sci.* **2016**, 7, 1430, DOI: 10.1039/C5SC03669K.
- [46] L. Zhang, Y. Gao, X. Ding, *J. Energy Chem.* **2017**, 26, 163, DOI: 10.1016/j.jechem.2016.09.003.

- [47] L. Alibabaei, B. D. Sherman, M. R. Norris, M. K. Brennaman, T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5899, DOI: 10.1073/pnas.1506111112.
- [48] M. K. Brennaman, R. J. Dillon, L. Alibabaei, M. K. Gish, C. J. Dares, D. L. Ashford, R. L. House, G. J. Meyer, J. M. Papanikolas, T. J. Meyer, *J. Amer. Chem. Soc.* **2016**, *138*, 13085, DOI: 10.1021/jacs.6b06466.
- [49] B. D. Sherman, D. L. Ashford, A. M. Lapides, M. V. Sheridan, K.-R. Wee, T. J. Meyer, *J. Phys. Chem. Lett.* **2015**, *6*, 3213, DOI: 10.1021/acs.jpclett.5b01370.
- [50] B. D. Sherman, Y. Xie, M. V. Sheridan, D. Wang, D. W. Shaffer, T. J. Meyer, J. J. Concepcion, *ACS Energy Lett.* **2016**, *2*, 124, acsenergylett.6b00661, DOI: 10.1021/acsenergylett.6b00661.
- [51] B. D. Sherman, M. V. Sheridan, K.-R. Wee, S. L. Marquard, D. Wang, L. Alibabaei, D. L. Ashford, T. J. Meyer, *J. Am. Chem. Soc.* **2016**, *138*, 16745, DOI: 10.1021/jacs.6b10699.
- [52] R. Brimblecombe, G. C. C. Dismukes, G. F. G. F. G. F. Swiegers, L. Spiccia, *Dalt. Trans.* **2009**, 9374, DOI: 10.1039/b912669d.
- [53] R. Brimblecombe, A. Koo, G. C. Dismukes, G. F. Swiegers, L. Spiccia, *J. Am. Chem. Soc.* **2010**, *132*, 2892, DOI: 10.1021/ja910055a.
- [54] X. Xiang, J. Fielden, W. Rodríguez-Córdoba, Z. Huang, N. Zhang, Z. Luo, D. G. Musaev, T. Lian, C. L. Hill, *J. Phys. Chem. C* **2013**, *117*, 918, DOI: 10.1021/jp312092u.
- [55] G. F. Moore, J. D. Blakemore, R. L. Milot, J. F. Hull, H.-E. Song, L. Cai, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Energy Environ. Sci.* **2011**, *4*, 2389, DOI: 10.1039/c1ee01037a.
- [56] E. A. Gibson, L. Le Pleux, J. Fortage, Y. Pellegrin, E. Blart, F. Odobel, A. Hagfeldt, G. Boschloo, *Langmuir* **2012**, *28*, 6485, DOI: 10.1021/la300215q.
- [57] C. J. Wood, G. H. Summers, C. A. Clark, N. Kaeffer, M. Braeutigam, L. R. Carbone, L. D'Amario, K. Fan, Y. Farré, S. Narbey, F. Oswald, L. A. Stevens, C. D. J. Parmenter, M. W. Fay, A. La Torre, C. E. Snape, B. Dietzek, D. Dini, L. Hammarström, Y. Pellegrin, F. Odobel, L. Sun, V. Artero, E. A. Gibson, *Phys. Chem. Chem. Phys.* **2016**, *18*, 10727, DOI: 10.1039/c5cp05326a.
- [58] L. Li, L. Duan, F. Wen, C. Li, M. Wang, A. Hagfeldt, L. Sun, *Chem. Commun.* **2012**, 48, 988, DOI: 10.1039/c2cc16101j.
- [59] M. K. Coggins, T. J. Meyer, in 'Photoelectrochemical Solar Fuel Production', Springer International Publishing, Cham, **2016**, pp. 513-548, DOI: 10.1007/978-3-319-29641-8\_13.
- [60] Z. Ji, M. He, Z. Huang, U. Ozkan, Y. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 11696, DOI: 10.1021/ja404525e.
- [61] N. Kaeffer, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou, V. Artero, *J. Am. Chem. Soc.* **2016**, *138*, 12308, DOI: 10.1021/jacs.6b05865.
- [62] P. B. Pati, L. Zhang, B. Philippe, R. Fernández-Terán, S. Ahmadi, L. Tian, H. Rensmo, L. Hammarström, H. Tian, *ChemSusChem* **2017**, *10*, 2480, DOI: 10.1002/cssc.201700285.
- [63] M. Bonomo, D. Dini, *Energies* **2016**, *9*, 373, DOI: 10.3390/en9050373.
- [64] D. A. Hoogeveen, M. Fournier, S. A. Bonke, X.-Y. Fang, A. J. Mozer, A. Mishra, P. Bäuerle, A. N. Simonov, L. Spiccia, *Electrochim. Acta* **2016**, *219*, 773, DOI: 10.1016/j.electacta.2016.10.029.
- [65] K. A. Click, D. R. Beauchamp, Z. Huang, W. Chen, Y. Wu, *J. Am. Chem. Soc.* **2016**, *138*, 1174, DOI: 10.1021/jacs.5b07723.
- [66] J. R. Swierk, N. S. McCool, C. T. Nemes, T. E. Mallouk, C. A. Schmuttenmaer, *J. Phys. Chem. C* **2016**, *120*, 5941, DOI: 10.1021/acs.jpcc.6b00749.
- [67] J. R. Swierk, N. S. McCool, T. P. Saunders, G. D. Barber, T. E. Mallouk, *J. Am. Chem. Soc.* **2014**, *136*, 10974, DOI: 10.1021/ja5040705.
- [68] P. Xu, C. L. Gray, L. Xiao, T. E. Mallouk, *J. Am. Chem. Soc.* **2018**, *140*, 11647, DOI: 10.1021/jacs.8b04878.
- [69] P. Xu, T. E. Mallouk, *J. Phys. Chem. C* **2019**, *123*, 299, DOI: 10.1021/acs.jpcc.8b11356.
- [70] G. Charles Dismukes, R. Brimblecombe, G. A. N. Felton, R. S. Pryadun, J. E. Sheats, L. Spiccia, G. F. Swiegers, *Acc. Chem. Res.* **2009**, *42*, 1935, DOI: 10.1021/ar900249x.
- [71] M. G. Gatty, S. Pullen, E. Sheibani, H. Tian, S. Ott, L. Hammarström, *Chem. Sci.* **2018**, *9*, 4983, DOI: 10.1039/c8sc00990b.
- [72] E. A. Gibson, *Chem. Soc. Rev.* **2017**, *46*, 6194, DOI: 10.1039/C7CS00322F.
- [73] D. Gust, T. A. T. A. Moore, A. L. A. L. A. L. Moore, *Acc. Chem. Res.* **2009**, *42*, 1890, DOI: 10.1021/ar900209b.
- [74] L. Hammarström, *Acc. Chem. Res.* **2015**, *48*, 840, DOI: 10.1021/ar500386x.
- [75] R. L. House, N. Y. M. Iha, R. L. Coppo, L. Alibabaei, B. D. Sherman, P. Kang, M. K. Brennaman, P. G. Hoertz, T. J. Meyer, *J. Photochem. Photobiol. C Photochem. Rev.* **2015**, DOI: 10.1016/j.jphotochemrev.2015.08.002.
- [76] S. Yun, N. Vlachopoulos, A. Qurashi, S. Ahmad, A. Hagfeldt, *Chem. Soc. Rev.* **2019**, *48*, 3705, DOI: 10.1039/C8CS00987B.
- [77] J. Desilvestro, M. Graetzel, L. Kavan, J. Moser, J. Augustynski, *J. Am. Chem. Soc.* **1985**, *107*, 2988, DOI: 10.1021/ja00296a035.
- [78] N. Vlachopoulos, P. Liska, J. Augustynski, M. Grätzel, *J. Am. Chem. Soc.* **1988**, *110*, 1216, DOI: 10.1021/ja00212a033.
- [79] P. Liska, N. Vlachopoulos, M. K. M. K. Nazeeruddin, P. Comte, M. Grätzel, M. Graetzel, M. Grätzel, *J. Am. Chem. Soc.* **1988**, *110*, 3686, DOI: 10.1021/ja00219a068.
- [80] R. Dabestani, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. E. Webber, J. M. White, **1988**, 1872, DOI: 10.1021/j100318a035.
- [81] M. Grätzel, P. Liska, US Patent, **1990**, 4927721. URL: <https://patents.google.com/patent/US4927721A/en>
- [82] M. K. Nazeeruddin, P. Liska, J. Moser, N. Vlachopoulos, M. Grätzel, **1990**, 73, 1788, DOI: 10.1002/hlca.19900730624.
- [83] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737, DOI: 10.1002/adma.201001703.
- [84] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382, DOI: 10.1021/ja00067a063.
- [85] A. Hagfeldt, B. Driksson, T. Palmqvist, H. Lindström, S. Södergren, H. Rensmo, S.-E. Lindquist, *Sol. Energy Mater. Sol. Cells* **1994**, *31*, 481, DOI: 10.1016/0927-0248(94)90190-2.
- [86] P. Bonhôte, E. Gogniat, S. Tingry, C. Barbé, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, *J. Phys. Chem. B* **1998**, *102*, 1498, DOI: 10.1021/jp972890j.
- [87] J. Koryta, J. Dvorak, L. Kavan, 'Principles of Electrochemistry', Wiley, Chichester, England, **1993**.
- [88] D. N. Blauch, J. M. Saveant, *J. Am. Chem. Soc.* **1992**, *114*, 3323, DOI: 10.1021/ja00035a025.
- [89] V. K. Thorsmølle, G. Rothenberger, D. Topgaard, J. C. Brauer, D.-B. Kuang, S. M. Zakeeruddin, B. Lindman, M. Grätzel, J.-E. Moser, *ChemPhysChem* **2011**, *12*, 145, DOI: 10.1002/cphc.201000819.
- [90] Y. Saygili, M. Söderberg, N. Pellet, F. Giordano, Y. Cao, A. B. Muñoz-García, S. M. Zakeeruddin, N. Vlachopoulos, M. Pavone, G. Boschloo, L. Kavan, J.-E. Moser, M. Grätzel, A. Hagfeldt, M. Freitag, *J. Am. Chem. Soc.* **2016**, *138*, 15087, DOI: 10.1021/jacs.6b10721.
- [91] V. A. Macagno, M. C. Giordano, A. J. Arvía, *Electrochim. Acta* **1969**, *14*, 335, DOI: 10.1016/0013-4686(69)85005-X.
- [92] S. M. Feldt, E. A. Gibson, E. Gabriellsson, L. Sun, G. Boschloo, A. Hagfeldt, *J. Am. Chem. Soc.* **2010**, *132*, DOI: 10.1021/ja1088869.
- [93] N. Papageorgiou, *Coord. Chem. Rev.* **2004**, *248*, 1421, DOI: 10.1016/j.ccr.2004.03.028.
- [94] J. Theerthagiri, A. R. Senthil, J. Madhavan, T. Maiyalagan, *ChemElectroChem* **2015**, *2*, 928, DOI: 10.1002/celec.201402406.
- [95] M. Wu, T. Ma, *J. Phys. Chem. C* **2014**, *118*, 16727, DOI: 10.1021/jp412713h.
- [96] 'Counter-Electrodes or Dye Sensitized and Perovskite Solar Cells', Volumes 1 and 2, Eds. S. Yun, A. Hagfeldt, Wiley-VCH, Weinheim, **2018**.
- [97] H. Ellis, N. Vlachopoulos, L. Häggman, C. Perruchot, M. Jouini, G. Boschloo, A. Hagfeldt, *Electrochim. Acta* **2013**, *107*, 45, DOI: 10.1016/j.electacta.2013.06.005.
- [98] Y. Saygili, M. Stojanovic, N. Flores-Díaz, S. M. Zakeeruddin, N. Vlachopoulos, M. Grätzel, A. Hagfeldt, *Inorganics* **2019**, *7*, 30, DOI: 10.3390/inorganics7030030.
- [99] R. Komiya, A. Fukui, A. N. Murofushi, N. Koide, R. Yamanaka, H. Katayama Technical Digest, 21st International Photovoltaic Science and Engineering Conference, Fukuoka, Nov. **2011**; 2C-50-08.
- [100] S. Hattori, Y. Wada, S. Yanagida, S. Fukuzumi, *J. Am. Chem. Soc.* **2005**, *127*, 9648, DOI: 10.1021/ja0506814.
- [101] L. Kavan, Y. Saygili, M. Freitag, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel, *Electrochim. Acta* **2017**, *227*, 194, DOI: 10.1016/j.electacta.2016.12.185.
- [102] J. Li, X. Yang, Z. Yu, G. G. Gurzadyan, M. Cheng, F. Zhang, J. Cong, W. Wang, H. Wang, X. Li, L. Kloo, M. Wang, L. Sun, *RSC Adv.* **2017**, *7*, 4611, DOI: 10.1039/c6ra25676g.
- [103] Y. Cao, Y. Liu, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel, *Joule* **2018**, *2*, 1108, DOI: <https://doi.org/10.1016/j.joule.2018.03.017>.
- [104] M. Freitag, J. Teuscher, Y. Saygili, X. Zhan, F. Giordano, P. Liska, J. Hua, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, A. Hagfeldt, *Nat. Photonics* **2017**, *11*, 372, DOI: 10.1038/nphoton.2017.60.
- [105] Y. Hao, W. Yang, L. Zhang, R. Jiang, E. Mijangos, Y. Saygili, L. Hammarström, A. Hagfeldt, G. Boschloo, *Nat. Commun.* **2016**, *7*, DOI: 10.1038/ncomms13934.
- [106] M. Freitag, Q. Daniel, M. Pazoki, K. Sveinbjörnsson, J. Zhang, L. Sun, A. Hagfeldt, G. Boschloo, *Energy Environ. Sci.* **2015**, *8*, 2634, DOI: 10.1039/c5ee01204j.
- [107] Y. Cao, Y. Saygili, A. Ummadisingu, J. Teuscher, J. Luo, N. Pellet, F. Giordano, S. M. Zakeeruddin, J.-E. Moser, M. Freitag, A. Hagfeldt, M. Grätzel, *Nat. Commun.* **2017**, *8*, DOI: 10.1038/ncomms15390.
- [108] J. A. Treadway, J. A. Moss, T. J. Meyer, *Inorg. Chem.* **1999**, *38*, 4386, DOI: 10.1021/ic990466m.
- [109] M. Hamburger, G. Kodis, M. D. Vaughn, G. F. Moore, D. Gust, A. L. Moore, T. A. Moore, D. Gust, T. E. Mallouk, *Dalton Trans.* **2009**, *1*, 9979, DOI: 10.1039/b912170f.
- [110] M. Hamburger, G. F. Moore, D. M. Kramer, D. Gust, A. L. Moore, T. A. Moore, *Chem. Soc. Rev.* **2009**, *38*, 25, DOI: 10.1039/B800582F.

- [111] G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda, O. Ishitani, *Chem. Commun.* **2015**, 51, 10722, DOI: 10.1039/C5CC02403J.
- [112] Y. Kou, S. Nakatani, G. Sunagawa, Y. Tachikawa, D. Masui, T. Shimada, S. Takagi, D. A. Tryk, Y. Nabetani, H. Tachibana, H. Inoue, *J. Catal.* **2014**, 310, 57, DOI: 10.1016/j.jcat.2013.03.025.
- [113] A. Bachmeier, S. Hall, S. W. Ragsdale, F. A. Armstrong, *J. Am. Chem. Soc.* **2014**, 136, 13518, DOI: dx.doi.org/10.1021/ja506998b.