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Review

Dye sensitization solar cells: a critical assessment of the learning curve

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Contents

Abstract

The learning curve for dye sensitized solar cells is analyzed and tentatively compared with the learning curve for classical solar cells. It appears that for one decade now the efficiency of nano-structured cells has been essentially stagnating despite significant research progress. This problem is analyzed and found to be mainly due to the exhausted exploitability of the surface roughness factor and the involvement of new mechanistic principles, which are scientifically still barely understood and therefore not well optimized. These are charge separation via irreversible kinetics and not via imprinted electrical fields, the role of metal-centered, coordination chemical electron transfer and of chemical back bonding of the sensitizer for increased reactivity and stability as well as the function of the front FTO contact as a vectorial, electron collecting interface. The parameters which determine long-term solar cell stability are also addressed. They will have to be explored in detail. Metal-centered sensitized electron transfer is definitely an advantage. In addition, the branching coefficient determined by the ratio of sensitizer regeneration and product formation is critically dependent on TiO_2 surface states, which determine degradation kinetics. The analysis includes solid-state dye sensitization cells, which are presently faced with even more problems concerning efficiency and stability than liquid ones.

Keywords: Dye sensitization cell; Ru complexes; Back bonding; Electron transfer; Dye photo-stability

1. Introduction

Dye molecules as light absorbers and electron transducing agents for energy conversion have shaped evolution via the process of photosynthesis and photo-sensoric mechanisms. Dyes have also significantly influenced the technical

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implementation and development of photography. Since 1968, after the discovery of dye sensitization of the photocurrents on semiconducting electrodes, dyes have also been used in electrochemical energy converting cells [1,2]. Light, via the light-absorbing and sensitizing activity of dyes, was found able to drive electrochemical cells for photoelectric power generation. The principal interest at that time was the demonstration that excited chlorophyll in photosynthesis could act as a sensitizing molecule for the photoelectrochemical turnover of electrons within the biological electron-transfer protein chain. The model systems of dye sensitization solar cells around 1970, operating with chlorophyll or chlorophyll derivatives, were therefore, "bionic" models, which attempted to mimic and reproduce the biological, physical, chemical processes of primary photon energy conversion involving chlorophyll and its derivatives [2,3]. The metal oxide electrode was intended to replace the electron-transfer protein chain. Since sensitization solar cells separated charge generation from charge transport, the quality of the material, which was sensitized, typically large band gap oxides, was not as critical as the quality of materials for classical photovoltaic cells, which have to provide good photo-response as well as good charge mobility within the same compound. But most early studies on sensitization were made with single crystal oxide samples because by eliminating grain boundaries and high concentrations of surface states the interpretation of the results became more transparent. However, even at that time, samples sintered from oxide powder were also used [1]. During the first years of sensitization solar cell research, many different dyes were tested and both, p- and n-type materials, were studied as substrates for electron or hole injection [4,5]. The effect of a redox system was investigated in detail as were questions of dye stability. It turned out that all dyes investigated at that time gradually degraded so inhibiting practical applications. In 1968 the dye sensitization solar cells generated, under conditions comparable to solar illumination, photocurrent densities of 0.5–1 mA/cm^2, equivalent to approximately 0.5% energy conversion efficiency. This motivated the outlook: "provided it is feasible to harvest light via photochemical reactions, the cell proposed here appears to promise optimal outputs. The effort which will have to be developed may however be substantial" ([1], p. 118 and repeated in Ref. [2]). Regardless of the obvious problems with the stability of organic sensitizers, the efficiency of dye sensitization cells was explored further by various researchers by investigating single crystalline and sintered oxide materials as substrates. Research papers, which should be specially mentioned, are those by Tsubomura et al., which showed an approximately 1.5% energy conversion efficiency (for light incident within the dye spectrum) for Rose Bengal sensitized zinc oxide ceramics [6]. Later, in 1980, the same group studied zinc oxide again and demonstrated an energy efficiency of 2.5%, also for light incident within the absorption spectrum of the sensitizer [7]. The redox system used was iodide/triiodide. Ruthenium complexes were also investigated during that period [8] but were not found to be particularly interesting. Apparently the electrolyte was not properly selected to allow the complex a suitable degree of interaction with the oxide. During this period copper complexes were also investigated as sensitizers for sintered oxide materials (ZnO) [9]. During the 1980s, a lot of different sensitizing dyes were investigated with respect to their photoelectrochemical properties. Amongst those also the sensitizer Rose Bengal together with the reducing compound hydroquinone were restudied on zinc oxide [10]. The results confirmed an effective quantum efficiency of close to 100% for this system. This matches the result with the same system obtained previously in 1968 [1]. Such a high quantum efficiency of course did not mean a high-energy conversion efficiency because the injection current was derived for a few dye monolayers on monocrystalline oxide material.

A significant improvement in the field of dye sensitization solar cells came, as is well known, in 1989, through the efforts of Grätzel and his research group [11,12]. To understand his contribution, it is necessary to reconsider the efforts made in the preceding years to reach higher energy conversion efficiencies with dye sensitization solar cells. To obtain an energy conversion efficiency of 2.5% (for artificial light within the absorption spectrum of the dye) [7] the surface roughness of the zinc oxide sample was systematically increased by adding aluminum. The relevance of surface roughness for the solar cell efficiency was clearly recognized as well as the advantage of using the iodide/triiodide redox couple. The experience made with various dyes with respect to their stability was, however, not at all encouraging so that the efforts were not continued. Even though the zinc oxide sinter material used can now be defined as a nano-material, as deduced from electron microscopic pictures published in the relevant manuscript [7], and even though the iodide/triiodide redox system was used, the cell did not yet motivate optimism.

In our opinion the significant advance made by Grätzel's group to improve energy conversion efficiency from lower than 2.5 to 7% was principally due to the following circumstances: Progress made with the preparation of the nano-structured TiO_2 [13] was combined with the use of a ruthenium complex, which was adequately bonded to the TiO_2 material. The same kind of ruthenium complex (but not identical) had been used before in 1980 [8] and even earlier [14] for sensitization but the selected aqueous electrolyte did not allow for an efficient adsorption to the oxide substrate. Grätzel's group took account of that and selected organic electrolytes for sensitization solar cells. It was the extraordinary performance of these Ru complexes, *cis*-X_2-bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium with X = Cl^-, Br^-, I^-, CN^-, or NCS, attached to nano-crystalline TiO_2 which caused the significant advance in 1991 [11]. The best results were obtained with the ruthenium complex with X as NCS (in the literature also shortly named R3 or Ru535). The jump in solar energy conversion efficiency

motivated significant optimism with respect to the feasibility of cheap and long-term stable dye sensitization solar cells. It was, however, not generally shared, first, because the cell included noble metals (ruthenium/platinum) and it had to be perfectly sealed because of its toxic organic components. Conductive glass is also a non-negligible cost factor. In addition, the expected long-term stability of the dye was deduced from spectroscopic and short-term photochemical evidence. It had not been tested in long-term operating dye sensitization solar cells.

In the nearly one and a half decades following the discovery of Grätzel's group, many research teams (approximately 80) have tried to improve and understand the dye sensitization solar cell. Many different dyes and transition metal complexes have been tested as sensitizers. Many types of electrolytes have also been examined including gel-polymer- and molten-salt-electrolytes [15–17]. Many new preparation techniques have been tried for nano-crystalline titanium dioxide [18–20]. Numerous spectroscopic analytical or electrochemical techniques have been applied to characterize nano-structured dye sensitization cells [21–23] and chemical components were added or replaced [24–26]. Further, in the search for the origin of the photopotential the SnO_2/TiO_2/electrolyte contact received special attention [27–30].

Efforts have been developed industrially to produce sensitization solar cells in a reproducible, professional way. The most significant effort appears to have been developed by INAP in Gelsenkirchen, Germany, by standardizing and carefully controlling all the steps for production of the dye sensitization solar cell. They succeeded in obtaining very reproducible solar cell prototypes. Nevertheless, the efficiency never exceeded a 7–8% limit and the long-term stability was not satisfactory for supporting straightforward industrial production effort. However, the technical efforts continue, for example, by Solaronix in Switzerland, by STI in Australia, the Ecole Polytechnique Federal Lausanne (EPFL), or the ISE and University Freiburg in Germany. They are supported by many scientific efforts to understand and improve the dye sensitization cell. Undoubtedly, Grätzel and his group, by making significant progress in a once stagnating field of research, have attracted and shared the creativity of many scientists.

The aim of this contribution is to analyze the learning curve for dye sensitization solar cells in order to discover possible weaknesses and deficiencies in research and development. The motivation is, of course, to try to push the field ahead by stimulating discussion. Comparing learning curves, the progress in efficiency over the years, for solar cells is not straightforward. Progress may depend on the number of researchers involved, on the availability of new materials, or on jumps in knowledge or creativity. It may be argued that silicon solar cells have received much more attention, especially from industry. But, interestingly, CdTe or $CuInSe_2/S_2$ (CIS) solar cells, which have received much less industrial attention show similar learning curves. The reason may be relatively simple. Industry concentrates on industrial prototypes, which require more adapted production strategies, the efficiency of which typically is 30% lower than the laboratory efficiencies shown in Fig. 1 (top).

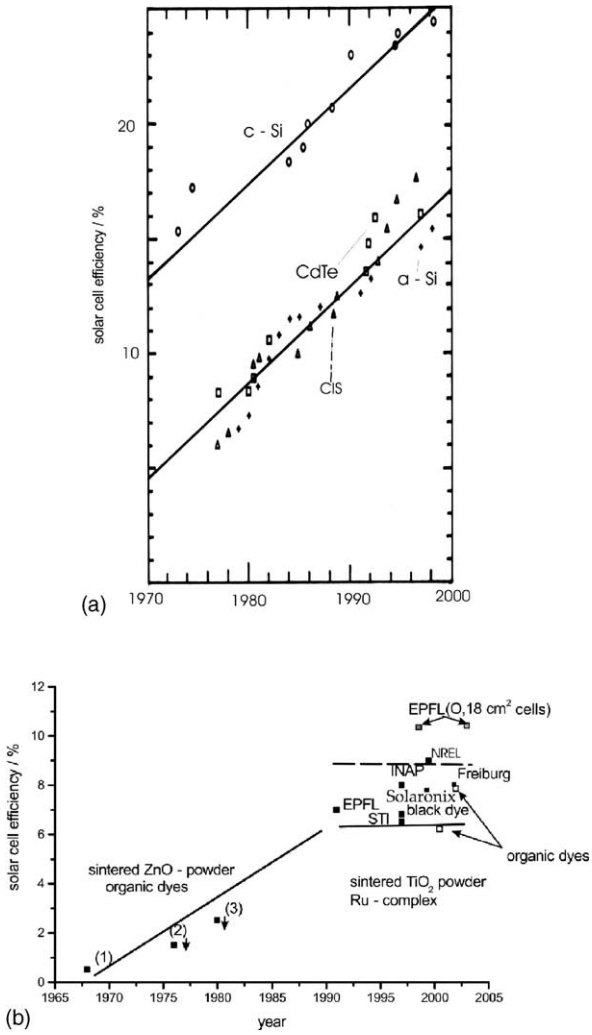

Fig. 1. Comparison of the learning curve for classical crystalline and thin layer laboratory solar cells (c-Si, a-Si, CdTe, CIS) with the learning curve for dye sensitization cells ((1), (2) and (3) correspond to Refs. [1,6,7] (the arrows indicate that corrected solar cell efficiencies are lower), the other abbreviations are explained in the text). It is seen that the learning curve for dye sensitization cells is nearly stagnating since the onset of significant research interest after 1991 (one exception is a very small cell from EPFL which may take advantage from a significantly reduced internal resistance for charge collection).

Analysis of research progress until now, in comparison with the development of other, classical, solar cells, demonstrates that the development of the dye sensitization solar cell is stagnating to some extent. This can be seen from the learning curve, which is depicted in Fig. 1 (bottom) and compared with that experienced for classical solar cells (c-Si, a-Si, CdTe, CIS). The development of the dye sensitization solar

cell first followed a learning curve somewhat slower than that found for classical solar cells, during its first two decades, when still only a few research groups participated. After 1991, the learning curve for efficiency practically stagnated in spite of the involvement of many research groups. The efficiency record of 10.4% obtained with a very small cell of area only 0.18 cm^2 remains a singularity produced by the EPFL group and apparently takes advantage of a minimal internal resistance due to small cell dimensions. Until now it could not be approached by other groups. It appears that for solar cells of cm^2 dimensions efficiencies of 7–8% are realistic, with cells, which reach 9%, being exceptions obtained under especially favorable circumstances [31]. In all efficiency measurements the temperature effect, the phenomenon that efficiency may significantly decrease with temperature, is not considered (when heating from 10 to 70 °C a silicon solar cell, for example, may lose one-third of its efficiency). Typically the measurements are performed at lower ambient temperature at conditions where the solar cell is not allowed to heat up.

The best sensitization cells with purely organic dyes apparently reached efficiencies of 6%, and more recently with coumarine and polyene sensitizers even 7.7% [32].

We emphasize that the learning curve is reasonably correct, for dye solar cell efficiencies in Fig. 1b, only for its later phase (starting with 1995) when efficiencies could be confirmed. Before, efficiencies were probably lower. Cell efficiencies measured with zinc oxide ceramics were not simulated solar cell efficiencies, but measured with laboratory light sources, therefore downward pointing arrows were introduced into Fig. 1 (bottom) to indicate effectively lower efficiencies. The earlier efficiency reports from the Lausanne group with TiO_2-based cells, on the other hand, sometimes communicated 10% and even more efficient cells [33,34], but later only confirmed with very small area cells. The solar cell costs were then estimated to be only 10% of the silicon cell costs [33], a too optimistic expectation for many researchers, given that encapsulation of classical solar cells is already more expensive and calculated for lifetimes of 20–30 years.

The aim of this contribution will be to find out why the learning curve is so flat and why technical progress is seemingly stagnating in spite of significant ongoing scientific activities. No effort will be made to provide a detailed reference list of dye sensitization research, since it can be obtained from reviews and the internet.

2. Parameters determining the learning curve

When considering the critical parameters which controlled the development of the dye sensitization solar cell during its first two decades, we may pin down maybe three essential factors: one is the molecular electronic quality of sensitizing molecules. The second is the quality of the redox system and the third is the surface area of the oxide material, which can be covered by a sensitizer. This task of optimization may have been completed by 1990 with the nano-structured titanium oxide material sensitized by a ruthenium complex in the presence of the iodide/triiodide redox couple in an organic environment. However, with the effort to increase the surface area of the oxide substrate to a maximum extent, the electrolyte started to penetrate the oxide substrate and to reach the front FTO-contact. Because of this electrolyte penetration, the electrical field largely disappeared from the electrolyte/nano-TiO_2 interface, but sensitization still continued to work. This was simply due to the largely irreversible properties of the iodide/triiodide systems. Electrons can easily be donated but the reverse reaction to reduce triiodide is very sluggish. Empirically, it turned out that the iodide/triiodide system is much superior to other redox systems of a similar redox potential ($Fe(CN)_6^{3+/4+}$, quinone/hydroquinone, $Fe^{2+/3+}$) so that all realistic wet dye sensitization solar cells today operate with iodide/triiodide only.

2.1. The role of kinetically determined charge separation

This situation of a disappearing electrical field is not just a coincidence but reflects a change of a fundamental solar cell criterion. An electric field imprinted into a semiconductor electrolyte interface has stopped being significant for charge separation. Instead, charge separation has become controlled by irreversible chemical charge transfer kinetics. Injected electrons from the sensitizer can, even in absence of a major electrical field, be efficiently collected and may diffuse towards the front contact of a solar cell. The interfacial properties of the TiO_2 nano-particles in contact with the iodide/triiodide redox system and improved by a pyridinium compounds allow the safeguarding and collection of injected majority carriers. The electrical field induced by iodide/triiodide in the front FTO contact however becomes critical for charge collection from the TiO_2 nano-structure. This contact has to remain highly vectorial in its properties for electron exchange with iodide/triiodide. This can be experimentally demonstrated, since the deposition of small islands of platinum on the front contact will immediately lead to a break down of solar cell efficiency. Platinum islands can catalyze the reverse reaction of electrons with triiodide, making the iodide/triiodide system more reversible and this apparently leads to a significant break down of solar cell efficiency. From these observations it may be concluded that the irreversibility of charge transfer at the nano-particles and at the FTO front contact of the dye sensitization solar cell critically determine solar cell efficiency. From this the hypothesis may be derived that microscopic kinetic irreversibility has gradually become a critical aspect of the function of dye sensitization solar cells.

This is a suitable moment to say a few words about irreversibility. Many processes in nature are, of course, irreversible, and accompanied by an increase in entropy. One example is diffusion. Photo-induced charge carriers may

diffuse away from the site of generation, but they may also diffuse back. They may also be transferred across an interface and temporarily be trapped in an acceptor state, a specific quantum state. But thermal activation may occur and produce a reverse reaction. In order to generate sufficient irreversibility in terms of charge separation classical solar cell structures take advantage of inbuilt electrical fields, which act upon electronic charge carriers in interfaces and junctions. They spatially separate negative and positive charge carriers and suppress recombination. TiO_2 nano-particles in dye sensitization solar cells do not allow for the formation of electrical fields due to their small size and due to the interpenetration with the electrolyte. Other kinetic mechanisms are required for irreversible charge separation to become efficient at such interfaces. They have to replace the function of an electrical field by providing a sufficiently irreversible exchange of electronic charge carriers across the interface or across a certain distance. If this conclusion would be wrong, and traditional mechanisms of irreversibility would be sufficient, dye sensitization solar cells should also work well with reversible redox couples besides the nearly exclusively used kinetically irreversible I^-/I_3^- system. Other nano-composite cells such as the PPV polymer/fullerene solar cell [35] also owe their reasonable solar cell efficiency (3–4%) to kinetic irreversibility. This is provided by the property of the fullerene to capture electrons much more easily than to re-donate it. This is not seen in the energy scheme usually applied for these cells, which just places the polymer donor level above the fullerene acceptor level to explain charge separation. Such a relative electron level position alone cannot be the basis of reasonably efficient solar cell. If another electron acceptor than fullerene with a similar position of electronic states but without the property of kinetic irreversibility is used instead, the efficiency collapses. It is for this reason why we attribute a high significance to the understanding of molecular electronic mechanisms which enhance kinetic irreversibility. Such mechanisms are ultimately also responsible for the efficient charge separation occurring in the photosynthetic membrane. The electron is separated over a certain distance from the hole and molecular kinetic mechanisms suppress the reverse reaction.

While this need to generate enhanced and selective kinetic irreversibility has been pointed out [36], only moderate research effort has been directed into this innovative aspect of nano-composite solar cell function. If this conclusion would not be correct, progress would already have led to a replacement of the I^-/I_3^- redox couple in dye sensitization cells, which due to the complex chemistry and photochemistry involved is a continuous source of technical troubles. The same is the case for the composite PPV polymer–fullerene solar cell, the efficiency of which critically depends on the fullerene which is not stable in the presence oxygen and light. But no replacement is in sight. Both the dye and the polymer solar cell are kinetically determined solar cells and an important limiting factor is the degree of kinetic irreversibility provided by the I^-/I_3^- redox couple and by the fullerene, respectively.

One possible reason why research on kinetic irreversibility is stagnating is simply that the classical Marcus and Gerischer approach for describing electron transfer at semiconductor interfaces is fundamentally a reversible one, which allows electron exchange in both directions, so that irreversibility is a more complex factor requiring the interplay of successive mechanisms. For the sensitization process, it has, for example, been suggested to involve, during the reverse reaction, poor overlap between the Ru d state of the oxidized Ru535 complex and the TiO_2 conduction band and the involvement of the inverted Marcus domain due to a large driving force [17]. But also following-up reactions and complicated relaxation processes have been put forward as arguments for kinetic irreversibility. As a close to equilibrium mechanism, the Marcus theory of electron transfer is not adapted for the exploration of highly irreversible, far-from-equilibrium processes. A far-from-equilibrium irreversible electron transfer theory has been proposed, which allows understanding highly irreversible electron transfer processes as self-organized mechanisms involving feedback processes [36,38–42]. Recently a non-linear correlation between interfacial electron transfer and charge carriers dynamics in the space charge layer has also been suggested for classical semiconductor interfaces. This equally requires a non-linear electron transfer theory [43], which describes electron transfer as follows.

While an electron or electron density cloud is being transferred, a change is induced in the molecular electronic environment, which alters the electron transfer properties within a feedback process. Mechanisms of this type can develop highly irreversible electron transfer processes. The feedback loop does not allow for an inversion of the process. Such types of mechanism, which need to be further explored in detail, should become implemented in the vectorial interfacial processes on the TiO_2 nano-particles. In other words if electron bridges with such oriented, self-organized properties would be identified and attached to TiO_2 nano-particles, this would result in kinetic irreversibility. It would work like a rectifying element. If an ordinary electron bridge would be attached, which allows reversible electron transfer according to Marcus theory, this would not be the case and additional mechanisms would be required to generate irreversibility.

To give a practical example of how irreversible electron transfer mechanisms are interpreted today, the remarkable one-directionality of electron transfer within the bacterial photosynthetic reaction centers should be mentioned. It is characterized by an array of short-range electron transfer reactions, evolving among chlorophyll and quinone moieties. The primary electron transfer process is accompanied by an extremely small reorganization energy, required for structural reorganization, of approximately $\lambda = 0.2\,\text{eV}$. At the same time it takes place at small free energy changes. This aspect is considered to be central for ultra-fast charge separation. Suppression of charge recombination on the

other hand is attributed to a large free energy change which drives electron transfer into the Marcus inverted region, which is expected to slow down electron transfer [44]. An alternative interpretation of photosynthetic charge separation has however also been published: It emphasizes that the electron transfer may be too fast for justifying reversible Boltzmann statistics as assumed in Marcus theory. It is proposed that during electron transfer, when electronic charge density is transferred, electronic feedback via specific amino acid bridges is possible which can be calculated to give synergetic, far-from-equilibrium electron transfer [45]. Photosynthetic charge separation is not only very fast and irreversible, but uses only one of two nearly equivalent molecular electron transfer branches. The interpretation of classical equilibrium electron transfer theory simply is that evolution carries a second useless branch as a souvenir from the ancient past. In contrast, the two branches make sense for far-from-equilibrium electron transfer theory. They simply reflect the two reaction branches originating from a bifurcation point. When the photo-excitation process occurs in this region near the bifurcation point, significantly enhanced instability is expected. This greatly facilitates irreversible charge separation. The reaction center may have evolved towards self-organized irreversible charge separation. Irreversible, far-from-equilibrium electron transfer is a phenomenon, which, according to the author's opinion, is not sufficiently understood and may offer a big potential for innovation. Also a key to more efficient nano-crystalline dye solar cells may be found in understanding and implementing highly irreversible kinetic charge separation.

Tentatively it may be concluded that one reason for the sluggish learning curve of dye sensitization solar cells is based in underestimating the challenge of kinetic irreversibility for nano-crystalline dye sensitization solar cells. Conditions of kinetic irreversibility just happened to arise for historical reasons because an optimal redox system (iodide/triiodide) was selected and maintained now for over 25 years.

2.2. A photogalvanic cell taking advantage of vectorial interfacial properties

To understand this phenomenon of kinetic irreversibility in relation to the entire dye sensitization solar cell function some remarks have to be made about the basic principles involved. A thermodynamic scheme for the function of dye sensitization solar cells was presented [2] as early as 1972. It explained these cells by analogy to ordinary redox batteries (as shown in Fig. 2) with the difference that light-induced redox reactions are involved. Depending on whether the sensitizer with the reducing agent or the sensitizer with the oxidizing agent is interacting with the large gap semiconductor, one gets a photo-induced electron injection or a photo-induced hole injection. As Fig. 2 shows, electrical energy can be gained when the photo-induced redox reaction is split up into two reaction components, which

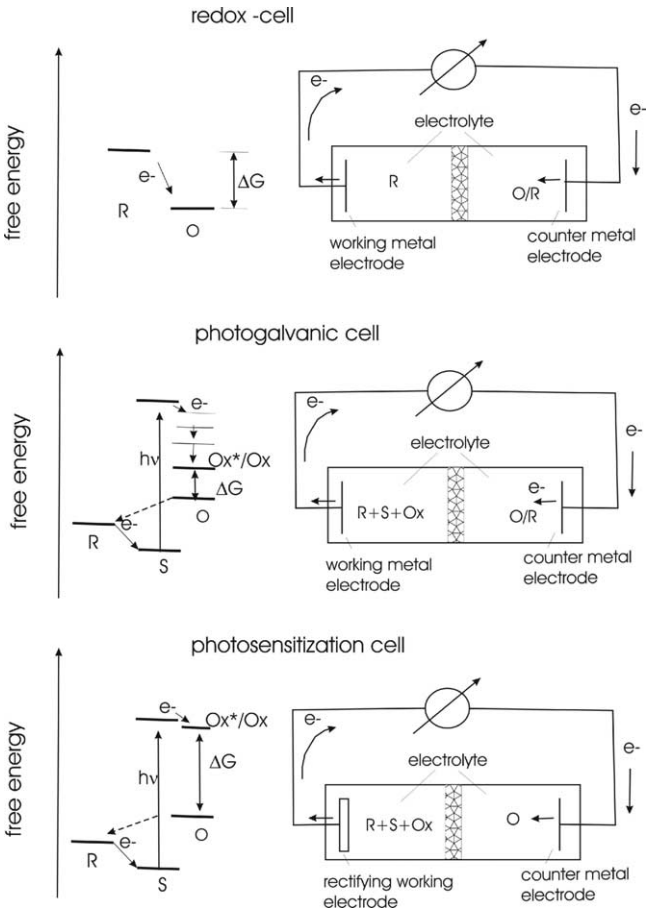

Fig. 2. Characterization of a dye sensitization cell via a redox systems in analogy to a redox battery (after [2]). This would correspond to a photogalvanic cell with an electrode, dipping into a photochemical environment, with the difference that the electrode interface is characterized by vectorial properties (electric field and/or kinetic irreversibility) (Ox* = electron injected oxide, Ox = oxide).

are allowed to proceed at separated electrodes. Photoreaction and electron transport is thus separated, which also allows the application of low-grade oxide materials including nano-crystalline particles. Once electrons or holes are injected to contribute to majority carriers they are not easily lost provided the surface of the nano-particles warrants a reasonable protection against electron exchange with the electrolyte via a sufficiently irreversible redox system. As we describe the dye sensitization solar cell principle, it would not be very different from the principle of a photogalvanic solar cell also described in Fig. 2. Such a photogalvanic cell works via a metal electrode dipping into a photochemically active system. By illuminating this system, the free energy will change thus inducing a difference in the electrode potential. It is, however, known that photogalvanic cells will not exceed an efficiency of maybe 1%. The reason is simply that a comparatively low concentration of reduced species is provided to the electrode. If this species is electron-injected TiO_2, which we can name TiO_2^*, the effectively detected concentration ratio of TiO_2^*/TiO_2 is low, because the electrode

has no vectorial property (in Fig. 2 the excited oxide (Ox^*) to non-excited oxide (Ox) ratio is indicated). Correspondingly the free energy to be gained is low. A dye sensitization cell with a conducting tin oxide (CTO) front contact, which is covered with a Pt Island, is an example for such a situation. The comparatively high solar cell efficiency breaks down because the electron transfer at the electrode becomes much more reversible. This has been shown [46] and can also be demonstrated via photocurrent imaging within one and the same dye solar cell by partial surface modification of the SnO_2 front contact with platinum islands or thin layers of other catalytic materials [47].

A sophisticated calculation has been published on the electronic function of the dye solar cell [48], which appears to model perfectly its power output characteristics numerically. Since the CTO contact to the TiO_2 was considered to be an ordinary metal, this model would not be able to describe the experimental fact that depositing Pt or other catalytic metals onto CTO (which does not change the metallic property of the contact) would lead to a break down of the solar cell. This means that the model is not able to describe one of its essential properties. The optimal fitting is apparently due to the multitude of adjusted parameters.

In order to become more efficient, nano-crystalline dye sensitization solar cells have to have the additional property of providing a vectorial front contact as an electrode. This front contact takes advantage of the irreversible properties of the iodide/triiodide redox system and of an CTO contact which in spite of a high electron conductivity still develops a narrow, maybe 2 nm thin, space charge layer. The reverse reaction of electrons from this front contact with triiodide is additionally suppressed kinetically. Nano-crystalline dye sensitization solar cells can therefore be characterized as photogalvanic cells, with the difference, that rectifying, vectorially behaving electrode contacts are used, which guarantee a significantly reduced reverse reaction and reduced reverse diffusion of electrons. In this way the electrode contact experiences an effectively higher concentration ratio of Ox^*/Ox (TiO_2^*/TiO_2) as indicated in the bottom scheme of Fig. 2.

These criteria have been considered in a mathematical model [36], which takes account of the interfacial charge transfer and of the surface recombination rate constants as well as the possibility that electrons can diffuse back into the nano-crystalline environment. The formula for photocurrent efficiency was given by

$$J_{ph} = q\frac{gI_L S}{k_4 I_3^-}\frac{1-(e^{-\alpha L_D}\sqrt{\Delta Uq/kT}/(1+\alpha L))}{1+(s_r/k_r)+(D/k_r L)\,e^{-\Delta Uq/kT}} \quad (1)$$

Here q is the electrical charge, g the excitation probability, I_L the photon flux, S the sensitizer concentration, I_3^- the triiodide concentration, α is the absorption coefficient, L_D is the Debye length and L the diffusion length. The rate constants k_4, k_r and s_r are explained in Fig. 3 and below. The quantity $(D/L)\exp(\Delta Uq/kT)$ in the denominator determines the back diffusion of electrons from the FTO/TiO_2 contact, which depends on the potential drop encountered in the TiO_2. Essentially, the TiO_2 layer has been treated as a photocathode donating electrons to a kinetically controlled front contact with the counter charges being transported by the electrolyte within the pores. In this formula, beside the concentration of the sensitizer, which critically determines the amount of photons absorbed and electrons injected, as well as the concentration of triiodide, which accounts for the recapturing of the injected electrons within the nano-structure two rate constants are most critical. These are k_4, which accounts for the reverse reaction rate of electrons from the nano-particles with triiodide and s_r, which accounts for the reverse reaction of electrons from the FTO front contact with the triiodide. These two rate constants (k_4 and s_r), which have to be kept very low, characterize the nano-structured dye sensitization solar cell as a system, which fundamentally depends on a significant irreversibility of interfacial charge transfer processes. Electron injection must occur at a high rate but the reverse reaction k_4 with the electrolyte must be very low. Charge transfer to the front contact via the rate constant k_r has to be very large but the reverse reaction with the electrolyte s_r has to be very low. Both low rate constants, k_4 and s_r, are determined by the irreversible kinetic nature of the I^-/I_3^- redox couple, that is by the complicated reduction chemistry of I_3^-. This redox couple was already found to be very useful for dye solar cells 25 years ago [7], as a consequence there has been little progress in enhancing irreversibility since. A lot of research concentrated on diverse dye solar cell parameters such as sensitizer optimization in the direction of increased light absorption and loading onto the oxide, charge transport in nano-structured environment, TiO_2 preparation or replacement of the organic electrolyte medium. The other key factors, the minimization of k_4 and s_r, affecting efficiency need in our opinion to be more thoroughly explored. The experimental factors reflecting it (the choice of the I^-/I_3^- redox system, and the choice of the F:SnO_2 contact as compared with the In:SnO_2 contact) had simply evolved through trial and error and were not further developed.

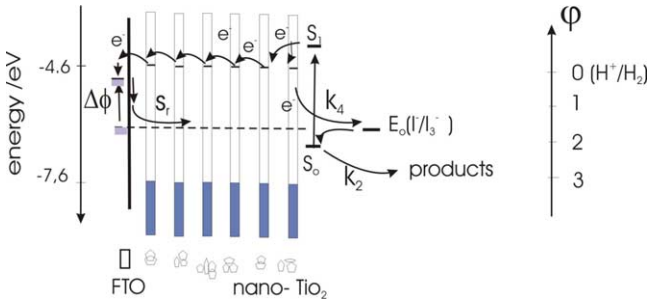

Fig. 3. Energy and kinetic scheme for nano-structured dye sensitization cell indicating the path of photo-injected electrons and the low rates for back reaction at the nano-particles (k_4) and at the front FTO contact (s_r).

The thermodynamic scheme of Fig. 2 (bottom), together with the requirement of a vectorial interface for efficient

charge collection at the front contact according to Eq. (1) define the nature of photopotential generation. Via the formula

$$U_{oc} = \frac{AkT}{q} \ln\left(\frac{J_{ph}}{J_0} + 1\right) \quad (2)$$

with A representing a diode factor, k the Bolzmann factor and J_0 the reverse saturation current, J_{ph} the photocurrent according to Eq. (1), the nature of the photopotential in dye sensitization solar cells is clearly defined. It is not generated as a purely 'dynamic' photopotential via a photo-induced potential change within the TiO_2 nano-structure (as discussed in Ref. [49]), since in this case the reverse reaction rate of electrons at the front contact s_r could be high (presence of Pt islands) and thus J_{ph} (as defined by Eq. (1)) very low. The photovoltage would largely collapse (medium scheme of Fig. 2). One needs in addition a vectorial front contact, which efficiently collects charge carriers while suppressing reverse reactions, making s_r and back diffusion of electrons into the TiO_2 nano-structured layer low. The vectorially behaving FTO front contact, in accepting electrons from the illuminated nano-TiO_2 is crucial for the generation of the photopotential, as also indicated by in situ electro-reflectance measurements on dye sensitization cells [46]. The observed electro-reflectance signals arise from the FTO contact, in presence of iodide/triiodide, and are logarithmically changed with light intensity. This means that the photo-induced electrochemical potential change in TiO_2 (as measured in a photogalvanic cell) together with the electron "collecting" vectorial properties of the front SnO_2 contact induce a shift of the Fermi-level in the latter from the I^-/I_3^- redox potential to the light intensity-dependent photopotential (2). The corresponding light intensity-dependent potential drop in the narrow space charge layer of SnO_2 is detectable by electrochemical electro-reflectance measurements. The optimization of the photocurrent J_{ph} in formula (2) is crucially dependent on slowing down the reverse reaction, as well as is the reduction of the reverse saturation current J_0. The same low kinetic rate constants, s_r and k_4, that maximize the photocurrent also minimize the reverse saturation current towards high photopotentials.

In our opinion the nano-structured dye sensitization solar cell depends on electron transfer irreversibility, both at the TiO_2 nano-particles and the FTO front contact. This most critical question, with respect to kinetic irreversibility, has not been properly addressed. As visualized for a simplified energy scheme of the dye sensitization solar cell in its nano-structured form (Fig. 3), the reverse reaction rate constants, both at the nanoparticles and at the FTO front contact, are the most critical parameters for the further development of dye sensitization cells.

2.3. The problem of dye performance

Over the past three decades, sensitizing molecules from nearly all known classes of chemical compounds have been investigated. Remarkably most turned out to be quite unstable so that they were excluded from solar cell applications. To these belong classical dyes like Rhodamine B or Eosine [1] as well as natural dyes like Chlorophylls and their derivatives [2,3] and many industrial dyes, which have been analyzed by chemical companies who took an interest in dye sensitized solar cell development. Transition metal complexes [9,11] turned out to be the most efficient and potentially stable sensitizers. However, with highly varying properties, ruthenium complexes remained the most attractive sensitizers, but only if the right electrolyte and the correct bonding to the oxide substrate are provided [11]. The same Ru535 (or N3) complex in the presence of aqueous electrolyte or in the absence of proper bonding to the oxide substrate turns out to be inefficient and unstable. The reason why transition metal complexes are suitable may be related to electron transfer mechanisms via d-states which are less critical for chemical bond breaking. For this reason attention has also been attracted to transition metal semi-conductor photoelectrodes whose energy bands are made from transition metal states (Fig. 4). So-called d-band semiconductors show high photo-stability in the presence of redox electrolytes, which can coordinate, i.e. chemically react with them, especially with the iodide/triiodide redox system. Interestingly the most stable semiconductor electrolyte interfaces ($FeS_2/I^-/I_3^-$, $MoSe_2/I^-/I_3^-$, $RuS_2/I^-/I_3^-$) show the same photo-induced redox chemistry as the Ru535–I^-/I_3^- system nearly exclusively used in dye sensitization solar cells. Iron disulfide crystals in contact with the iodide/triiodide system (Fig. 4, left) still showed no signs of photo-corrosion after the turned over photoelectrical charge should have consumed the crystal 17,000 times [50,51]. The explanations applied for d-band semiconductor interfaces, reacting with suitable electron donors [52] may, therefore, tentatively be transferred to the explanation of the efficiency and stability of ruthenium complex–iodide/triiodide interactions. The mechanisms are of a coordination chemistry nature. The interaction is very specific, leaving little room for undesirable side reactions. In contrast to other sensitization molecules not involving

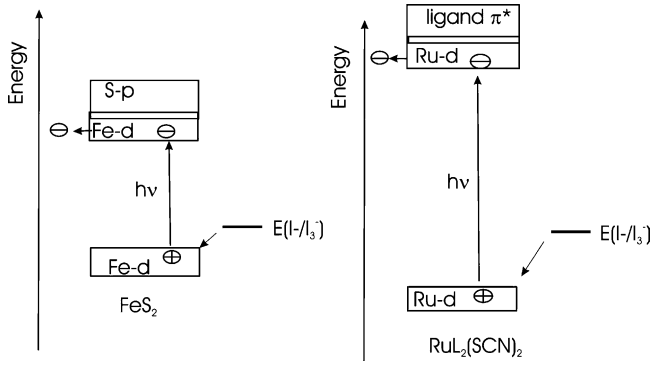

Fig. 4. Comparison of metal-centered electron transfer with Ru535 and d-band semiconductor electrodes (MoS_2, WS_2, FeS_2, RuS_2). In both cases selective coordination chemical electron transfer mechanisms lead to a significant increase of stability.

coordination chemistry, there are fewer chances for undesirable side reactions and for the splitting-up of molecules. Interestingly Fe^{2+} as electron donor in the same concentration as I^- neither generates as high photocurrents with FeS_2 nor guarantees a similar degree of photo-stability. It appears to be necessary that the electron donor is directly involved in a coordination reaction. Metal-centered electron transfer reactions are, therefore, the preferred process for photo-induced charge transfer at sensitized oxide electrolyte interfaces.

Research should also be aimed at increasing the optical extinction coefficient of sensitizers, so that dye solar cells could be made thinner and thus more efficient because of reduced transport losses in the nano-porous environment.

2.4. Sensitizer stability

One of the big accomplishments of Grätzel and his group was the identification of physical–chemical conditions, which allowed Ru complexes to tolerate a surprisingly large number of sensitization cycles. This is confirmed now. But is the number of electron transfer cycles as high as proposed? Since industrial efforts started in dye sensitization solar cell development, it was claimed that the ruthenium complex can survive 10^8 electron transfer steps and would therefore be stable for 20 years [53]. These conclusions were apparently derived from open-circuit experiments, performed with dye sensitization solar cells, illuminated with high laser light intensities. In contrast, when photocurrent imaging techniques were applied to selectively illuminated dye sensitization cells, clear photo-degradation was observed. As Figs. 5 and 6 demonstrate, photo-degradation is limited to selectively illuminated areas of a dye sensitization cell and depends linearly on the light intensity. Remarkably in some samples this degradation turned out to be already significant during the first days and weeks of illumination and decreased later on. Since no other factors, which could have been involved in photo-degradation, could be identified, the sensitizer was definitely found to be responsible [54–56].

As photocurrent imaging allowed much faster investigation of dye sensitization solar cells it was rapidly discovered

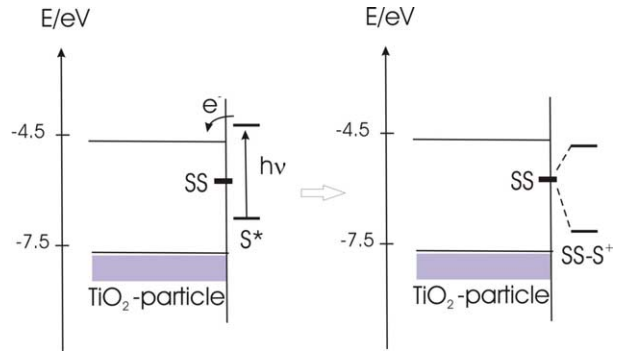

Fig. 5. Energy scheme visualizing the interaction of the oxidized sensitizer with a surface state. Left scheme shows electron injection, right scheme shows reaction of oxidized sensitizer with surface state.

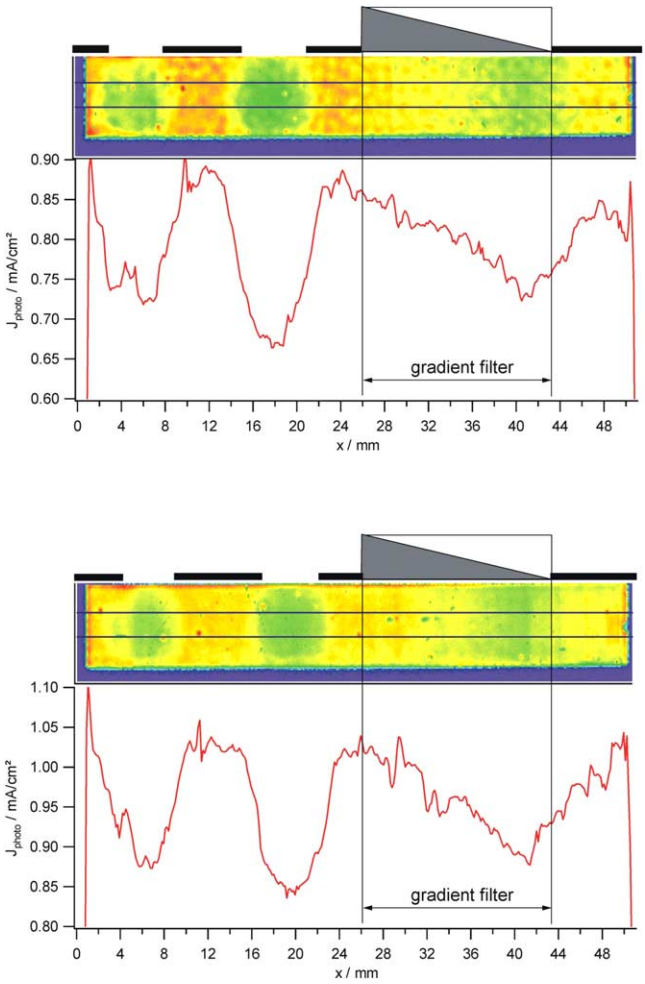

Fig. 6. Photo-degradation patterns observed with long-term illuminated dye sensitization solar cells (Ru535 or N3) selectively illuminated for 59 days through circular openings or through a graded absorption filter. Below, the photocurrent profiles are shown [56,57].

that not all areas of otherwise uniformly prepared cell surfaces were equally concerned by degradation. There were areas, which clearly showed lower degradation. A study of this phenomenon pinpointed surface states as the factor, which, in combination with adsorbed sensitizer molecules, was critically responsible for degradation. The stability of dye molecules apparently depends on the specific adsorption sites. There are adsorption sites where dye molecules have a greater chance to degrade and others where they have a smaller chance. It turned out that this conclusion is not a new one. Already in 1971, when chlorophyll molecules were studied as sensitizers on zinc oxide single crystals, this phenomenon was detected and characterized [3]. Some molecules photoreacted rapidly, others slower and the rest very slowly so that it could be concluded that the adsorption sites were responsible for the stability behavior. Interestingly it turned out that photocurrent degradation is much more efficient than a parallel decrease in light absorption of the dye solar cell, which is also detectable (the bottom picture in Fig. 6 is a video picture showing a patch in transmitted light

where selective illumination took place). The reason must be that most non-injecting oxidation products may also absorb light in the spectral region of the Ru535 complex. This has actually been confirmed with HPLC chromatographic techniques [57]. The photo-degradation products obtained with retention times clearly different from that of the Ru535 mostly had absorption spectra in the visible spectral region and sometimes quite similar to that of the Ru535 complex.

A few dye sensitization solar cells, which were investigated in our laboratory under simulated solar light over a long period (3626 h), produced a very small photocurrent, because soon after the start, the I^-/I_3^- system became unstable by producing iodate so that the electrolyte was bleached. Nevertheless, after a long illumination period, photocurrent images could be produced because the low cell current generated by the scanning laser spot could be supported by the cell. Surprisingly no photo-degradation patches were observed in this case [56]. This means that when no current is drawn from the dye sensitization cells, the degradation is significantly lower and not easily detectable. This observation explains why the high turnover number of 10^8 electrons came into discussion. It was derived from simulated experiments in the absence of photocurrent flow. Such conditions are not realistic for dye solar cell operation. A simplified formula derived to explain the time period during which the efficiency of a dye sensitization solar cell decreases to 50% shows (relation (3)) that the decrease in half-lifetime is inversely proportional to the photocurrent intensity J_{ph} and it increases, as more sensitizing molecules S_0 are present in the solar cell [16]:

$$T_{1/2} = \frac{0.67 S_0 F}{J_{ph}} \frac{k_3 I^-}{k_2} \tag{3}$$

where k_3 is the rate of sensitizer regeneration, k_2 the rate of product formation, and I^- the concentration of iodide. The lifetime is thus found to be proportional to the so-called branching coefficient k_{br}. The branching coefficient is a ratio of the regeneration rate of the sensitizer (defined by the product of the rate constant for electron transfer to the oxidized sensitizer times the concentration of iodide, the reducing compound in the electrolyte) and the rate constant for product formation (4):

$$k_{br} = \frac{k_3 I^-}{k_2} \tag{4}$$

Thus the stability increases, the more efficiently the sensitizer is regenerated and decreases with the rate of formation of the Ru(III) interfacial complex. It was a remarkable observation that the rate of product formation k_2 is not simply a homogenous rate constant, for example the rate of irreversible oxidation of the Ru535 complex. It is in fact an interfacial rate constant, because the Ru complex is adsorbed to TiO_2 nano-particles. But this interfacial rate is also dependent on the nature of the adsorption site of the sensitizer, that is on the nature of surface states involved. Where the chemical bonding is optimal, the oxidized sensitizer may survive until it is regenerated. Where it is perturbed and non-ideal, the oxidized sensitizer may irreversibly react. This is schematically shown in Fig. 5. Therefore the branching coefficient will be inversely proportional to the concentration of unfavorable surface states S_{ST} that may increase the sensitizer's irreversible reactivity.

$$k_{br} = \frac{k_3 I^-}{k_2' S_{ST}} \tag{5}$$

The half-lifetime of a sensitization solar cell will therefore be critically dependent on the presence of surface states S_{ST} which generate inferior survival periods for oxidized, adsorbed sensitizer molecules. This phenomenon explains not only why there is an increased degradation at the beginning of a long-term experiment, when still abundant sensitizer molecules are adsorbed on unfavorable surface states, but also why the rate of degradation is sometimes quite inhomogenously distributed over a sensitization cell.

Because of the turnover of sensitizer molecules, degradation is directly related to current flow. This has been confirmed by illuminating a sensitization cell via a linearly graded filter. A laterally linear degradation was measured demonstrating that degradation is proportional to light intensity (Fig. 6). If a solar cell is studied with respect to long-term stability, it must therefore be considered that a 1% efficient solar cell will be 10 times more stable than a 10% efficient solar cell. Sensitizer degradation will, therefore, be directly related both to concentration of surface states and to the passage of charge, which will generate oxidized sensitizer molecules. Indeed, when photocurrent profiles of inhomogenously photo-active sensitization cells are studied in dependence of illumination time, it is observed that photo-degradation proceeds at a higher rate in the areas of high photocurrent density (high efficiency) [56]. As a consequence the photocurrent profiles taken through photocurrent images are smoothed out.

In aqueous environments, the Ru535 complex proved neither to be efficient nor stable. In homogeneous organic photochemical environments, the same Ru535 complex is also not stable. Illuminated Ru complexes may only tolerate up to 200 electron transfer cycles in homogenous liquid environment. This tendency that non-adsorbed Ru complexes are highly unstable was confirmed recently with HPLC chromatographic studies [57]. Only when the ruthenium complex is well bonded to TiO_2 interfaces, does it show reasonably good performance. This definitely means that the interfacial bonding of the ruthenium complex to the sensitizer substrate is of most critical importance. When after prolonged simulated solar illumination the ruthenium complex is extracted and chromatographically analyzed, modified ruthenium complexes are identified with clearly different retention time and spectral characteristic different from Ru535. However most still absorb light in the visible spectral region [57]. This explains why the photo-induced decrease of the photocurrent of the dye sensitization cell does not match the decrease of light absorption. A 10–20% photocurrent

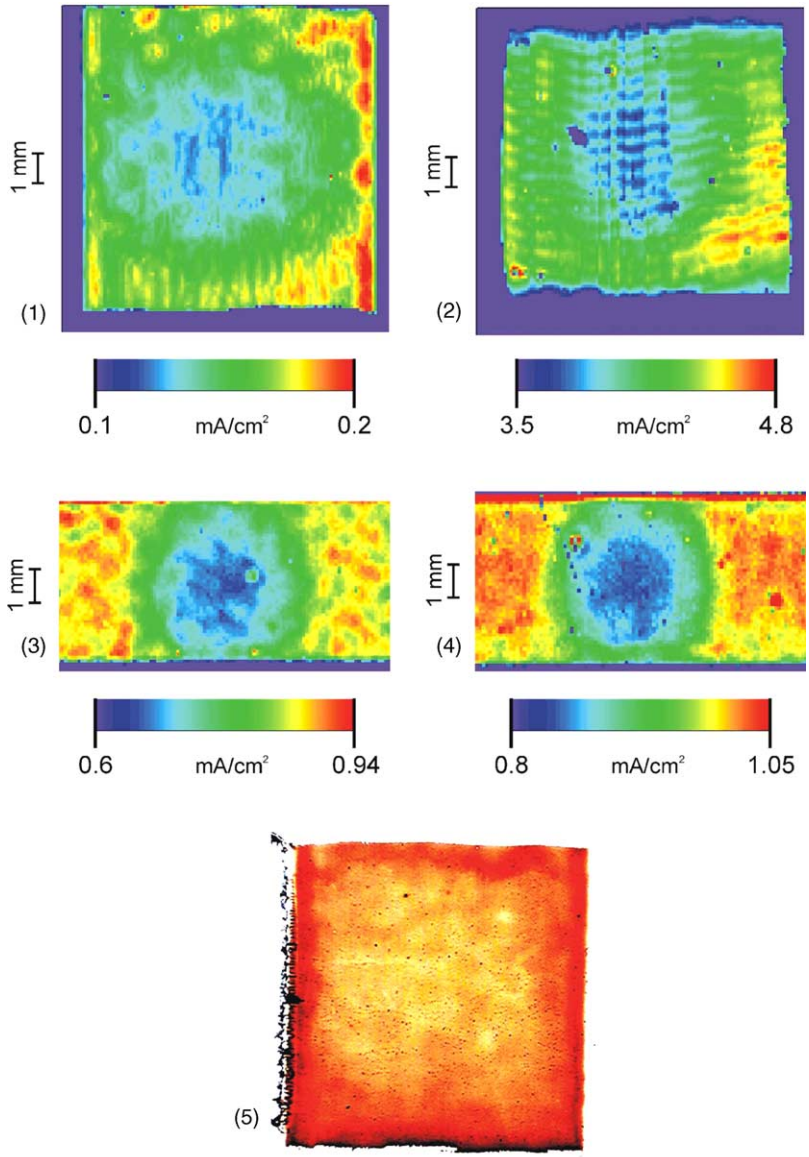

Fig. 7. Photocurrent images of selectively illuminated dye sensitization cells (Ru535) after prolonged illumination with simulated solar light [56]. Cell 1: 54 days; cell 2: 14 days; cells 3, 4: 52 days. Bottom picture 5: shows video picture of a photo-deteriorated cell 1 in transmission. The circular illuminated spot is visible [56].

decrease produced on a circular spot (Fig. 7, top 4 images) can be seen with the eye in transparency (Fig. 7, bottom picture), but may only correspond to an absorption change difference of one or a few percent, because oxidation products still absorb visible light, whereas they apparently cease functioning as efficient sensitizers. HPLC chromatographic results did not depend on the chemical extraction procedure, which was tested with the original Ru535 complex.

Since oxide interfaces and especially the interfaces of oxide nano-particles are far from being perfect one should expect a wide variation of all types of adsorption conditions. In other words, this means that there are obviously Ru535 molecules, which are optimally adsorbed and chemically bonded to the interface via their carboxyl groups and there will be others, which are only partially bonded or simply adsorbed in an unfavorable way. The conclusion must be that the photo-degradation of ruthenium complexes, observed with photocurrent imaging techniques is related to the presence of unfavorable adsorption sites. A scheme visualizing some possible sites for photo-degradation of Ru535 on the surface states of TiO_2 is shown in Fig. 8.

Altogether it was estimated that the Ru535 sensitizer may reach a turnover number of 10^7 rather than 10^8 as originally projected [36]. This would mean that the half degradation time for efficient dye solar cells would be closer 2 years and not 20 years. The theoretical explanation sketched clearly indicates that there is room for improvement of dye sensitization cells. With respect to the branching coefficient (relation (5)), it is evident that one would have to search for sensitizer modifications and electrolyte environments, which

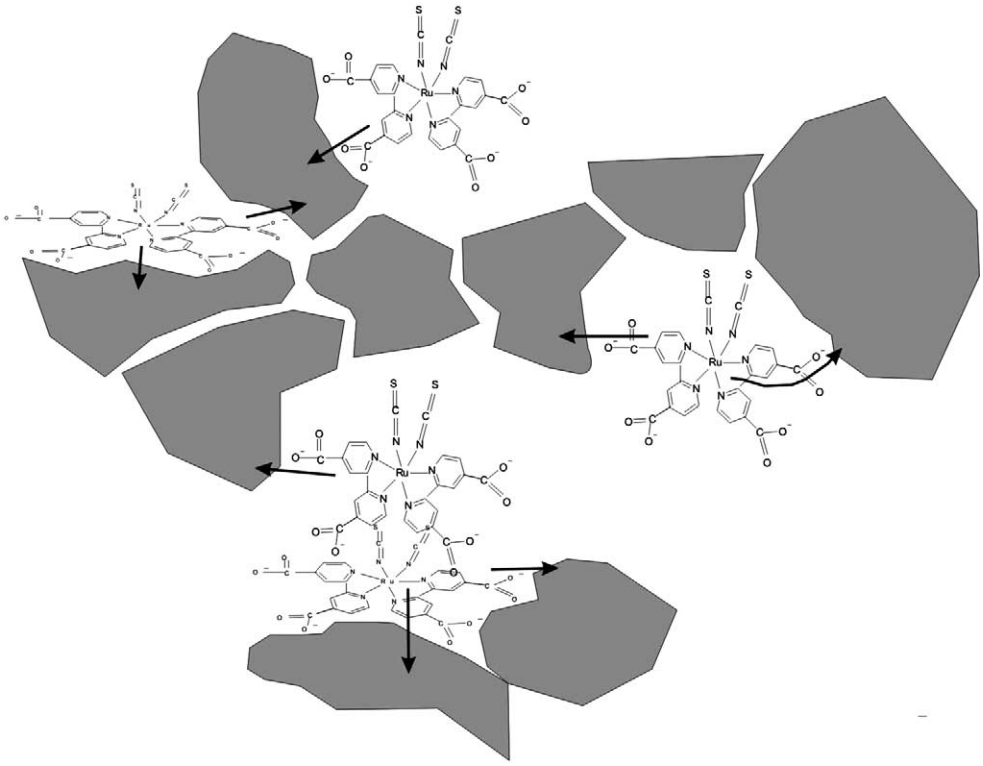

Fig. 8. Scheme showing how oxidized Ru535 sensitizer may be attached to different adsorption sites allowing different injection mechanisms and exposing the oxidized species to different interfacial chemical reactivity.

allow a higher rate of regeneration and only permit a lower rate for product formation. Also research on handling still higher concentrations of reducing agent (I^-) and surplus amounts of sensitizer could be rewarding. In addition, one has, of course, to find out the nature of surface states, which facilitate fast degradation processes. This means that surface states will have to be produced and modified to learn about their nature and properties. It is expected that differently treated TiO_2 substrates will produce different long-term stability properties of the sensitizer in otherwise identically prepared dye sensitization cells.

Now the question should be discussed, why does this Ru535 (N3) complex provide such favorable bonding conditions, when compared with other sensitizer molecules. Generally it has been demonstrated that it is necessary to attach a sensitizer to the solid through specific functions on the chromophore (carboxyl and phosphonate groups on the dye have been shown to work well in the role of binding to Ti atoms). Variants of ruthenium complexes have been investigated with different numbers and locations of these linking functions. The ultimately used standard ruthenium complex Ru535 performed better than simpler complexes [58]. Organic dyes attached with a single carboxyl linkage, such as tested for a merocyanine dye, did not perform well. However trimethine and pentamethine dyes with two carboxylic acid functions attached well and produced reasonable photocurrents, in one case comparable to the Ru535 (or N3) complex [58]. This was not surprising, as these cyanine dyes also have shown good performance in silver halide photographic emulsions. However, in no case has it been demonstrated that purely organic sensitizers performed comparable, in the long-term, with the Ru535 and comparable Ru complexes. Combinatorial research on long-term stability performed in our group supported the conclusion from other groups that organic dyes are much more susceptible to oxidative degradation than Ru metal complexes [56]. Tentatively it may therefore be concluded that high-quality bonding of the sensitizer to the oxide substrate is a necessary but not sufficient condition for good performance in dye sensitization solar cells.

2.5. Electron injection rate

Electrons are transferred by the sensitizer to the TiO_2 in time windows down to 20 fs [59,60–62], much faster than expected for thermal equilibration (non-adiabatic) processes. Electron injection into TiO_2 is therefore considered to occur in the adiabatic limit [63,64]. The situation is even more complicated as the same Ru535 (N3) dye with the same carboxyl groups apparently showed a much slower injection rate in the 10–100 ps time window into other oxides such as SnO_2 and ZnO [65,66]. A high injection rate cannot easily be a warranty for stability of resulting oxidized sensitizer for the product will have no memory of the injection process. The effect remains to be explained why the Ru535 complex is much more stable than other sensitizers and why

its stability critically depends on the bonding with the TiO_2 surface. How can quite weak peripheric bonding (order of magnitude 50 meV, for ester bond 1–2 eV) anyway guarantee photochemical stability, which is not at all warranted in homogeneous solution or during still weaker or more unfavorable adsorption of the Ru535 sensitizer to TiO_2? It would have to be concluded that the carboxyl bonding significantly increases the lifetime of the oxidized sensitizer molecule. Compared with a homogeneous reaction the lifetime improvement should at least occur by a factor of 100–1000. This is not easy to explain and needs careful consideration. A published opinion is that this is due to the rapid nature of the interfacial redox process. The rate constant for ligand substitution from the excited state is estimated to be more than 10^9 times smaller than that for electron injection and the reactivity of Ru(III) (to form a sulfur-deficient complex which is still expected to be a good sensitizer) estimated to be at least 10^8 times slower than the reduction by iodide [53].

As already mentioned the same sensitizer bonded to ZnO in a way analogous to TiO_2 is clearly less stable and apparently injects at a slower rate. Why should the oxidized Ru complex have a memory of the electron injection mechanism. Our experimental studies clearly show that the long-term dye photo-degradation seen in photocurrent imaging experiments is due to the instability of the oxidized dye, since photo-degradation is not seen when negligible photocurrent is passing through the solar cell due to an unfavorably high internal resistance [56]. Assuming that the oxidized Ru complex has a lifetime of 1 μs, it should not make a difference for stability whether the injection occurs in 20 fs or in 20 ps. If the special bonding of Ru535 to TiO_2 does not exist, the ruthenium complex degrades relatively easily. This results from numerous published experiments from homogeneous photocatalysis research and from recent chromatographic studies performed with illuminated Ru535 in organic solvents in our group [57]. It may be tentatively concluded that the special bonding situation of Ru535 molecules allows, after electron transfer, more order to prevail in the oxidized sensitizer species adsorbed on TiO_2. Other sensitizing molecules, subject to more unfavorable bonding conditions, start to react irreversibly and degrade more easily. Is it possible to stabilize or even decrease entropy temporarily and locally during a photoreaction? This question has not yet been discussed even though significant knowledge in coordination chemistry electron transfer has been accumulated for dye sensitization cell function [67,68].

2.6. Photoreaction and entropy turnover

Why is the Ru535 complex photochemically so exceptionally stable when properly bonded to TiO_2 and why is it quite reactive when non-bonded or very weakly bonded? The conclusion must be that the peripheric carboxyl bonds between Ru535 and TiO_2 are controlling stability. Our feeling is that they are too weak to significantly affect the bonding structure of the Ru complex. But the problem of sensitizer stability is a key problem for the commercialization of dye solar cells. The longer the sensitizer survives the cheaper will be the technology. Ultimately, a way will also have to be found to replace the Ru with more available transition metals. On the other hand there are opinions which maintain that very little Ru is needed and that the stability of the Ru complex is sufficient [53].

Thermodynamically a more stable molecular complex maintains a state of more reduced entropy. The question we raise is therefore a question related to entropy turnover. What can be said about entropy turnover during photochemical reactions? During most photo-induced reactions, entropy in the molecular environment, disorder, increases. This occurs parallel to entropic heat production always arising from photon energy conversion. This means, bonds are broken and new reaction products are formed. Irreversible thermodynamics tells us, however, that the increase in entropy is not always a necessary consequence of energy turnover, at least locally. If suitable feedback processes would exist, entropy could locally be exported and decreased at the expense of an overall entropy production so that order could be established temporarily. On a molecular basis, this possibility of dynamic entropy export has been little explored. However, it has been theoretically shown that far-from-equilibrium self-organized synergetic electron transfer can occur, provided molecular electronic feedback loops are present [42]. This means, when the electron is being transferred, that something should change which further increases the electron transfer probability. This feedback can be very fast and electronic, as expected for Ru535, but it can also be slow and based on molecular rearrangement. The consequence is self-organization. There is a reduction of entropy or a build-up of order until other reactions start to dominate. As an example from photobiology, the molecule bacteriorhodopsin has been discussed [69]. Upon absorption of a photon bacteriorhodopsin is known to perform a quite complex photoreaction cycle [70]. During the light-induced conformational change of this molecule 150.84 $kJ\,mol^{-1}$ of heat is released in addition to the energy content by the photon (205 $kJ\,mol^{-1}$) [71]. The free energy stored must, therefore, take the form of decreased entropy of $-300\,J\,mol^{-1}\,K^{-1}$ in the formation of the meta-stable state for the net energy change to be possible. This large entropy decrease implies a substantial increase in molecular order. It could be compared with the entropy change in the opposite direction that accompanies the unfolding of a protein like lysocyme. The pronounced decrease in entropy during the bacteriorhodopsin cycle has been confirmed and reinvestigated [71b]. The ability of bacteriorhodopsin to reduce its entropy upon photon-absorption is reflected in its extraordinary chemical stability. Because of its photochromic properties and its favorable stability properties over many years of use it has seriously been considered as absorber for optoelectronics. The capacity of this molecule to export entropy has been explained and

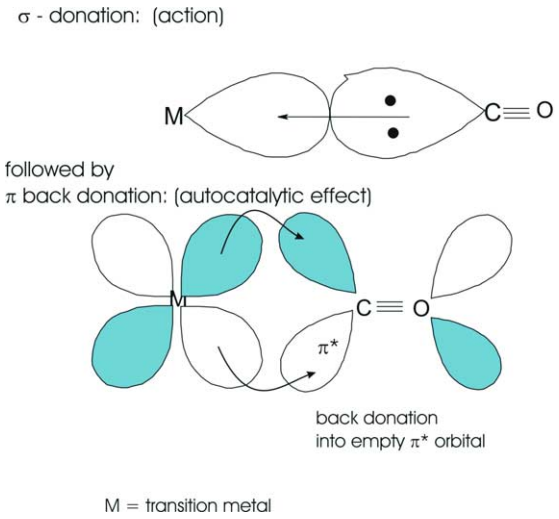

Fig. 9. Scheme characterizing back bonding as a feedback or autocatalytic process with dative σ bonding (top) followed by π back bonding with empty π* orbitals of the donor, reinforcing the σ bonding.

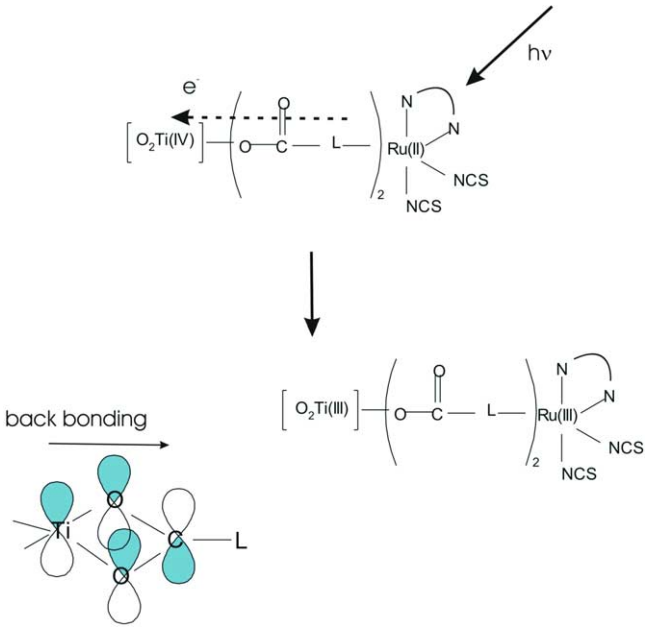

Fig. 10. Tentative application of back bonding concept to Ru535–TiO_2 interaction. The Ru535 complex, excited via a metal to ligand charge transfer transition, donates electronic charge density via a ligand π* orbital to Ti(IV) reducing it towards Ti(III) which thus becomes able to engage in some back bonding with the Ru535 complex, which in turn improves the transfer of electron density from the ligand π* orbital. The process is thus autocatalytic.

linked to autocatalytic self-organization also evidenced by oscillatory photochemical properties [72].

The hypothesis may now be advanced that the Ru535 complex also has the capacity to temporarily export entropy as a consequence of photoabsorption and electron injection. This could, on the basis of calculated phenomenological models [42], explain both extremely fast electron transfer and the increased chemical stability of the absorbed oxidized R535 complex. A necessary precondition for such self-organized transient processes would be a suitable feedback mechanism. During the electron transferring photoprocess between Ru535 and TiO_2 something must occur to improve it. Our attention was attracted to the well-known back bonding mechanism known from metal organic complexes (Fig. 9). A carbon–metal σ-dative bond is reinforced by a donation of electrons from the π-type, d-orbitals of the metal to empty π* orbitals of the carbon monoxide ligand. Some models indeed describe more importance to the π-type "back bonding" than to the σ-donation. This bonding mechanism is truly synergetic or autocatalytic, because initial bonding is producing a feedback, which is amplifying the bonding. This feedback produces a drift of metal electron density, referred to as "back bonding" which enhances the acceptor strength of π orbitals. The effect of σ bond formation strengthens the π bonding and vice versa. In a simplified way, this situation is shown in Fig. 9.

Back bonding mechanisms have been discussed for numerous ruthenium complexes. Can they also be attributed to the Ru535 complex interacting with TiO_2 interfaces? As Fig. 10 shows, the Ru535 complex interacts with surface Ti(IV). In this case the Ti($3d^0$) would not allow a back interaction with the ruthenium complex. However, when the excited electron is being transferred from the excited Ru535 complex, Ti($3d^1$) builds-up. In octahedral symmetry e_g and t_{2g} symmetries result. The additional electron of Ti(III) will go into a formally non-bonding t_{2g} orbital. It can however be delocalized back into empty orbitals of the ligands of the Ru complex. Such a back donation or back bonding would lower the energy of the orbitals involved. One could, therefore, imagine that during photo-induced electron transfer the electron density via the di-carboxyl bipyridyl ligand donating bond will increase towards formation of Ti(III) with a subsequent increase of π-back bonding with the Ru535 complex, which will further facilitate the transfer of electron density towards TiO_2. In this way an autocatalytic and thus temporarily self-organized electron transfer process would be imaginable. It may have the inherent potential to locally and temporarily increase order equivalent to a decrease or export of entropy. This order could do both, increase the rate of electron transfer and increase the survival period of the oxidation product. This has been demonstrated through phenomenological calculations [37–42]. While this proposal is for the moment hypothetical, as far as the attached Ru535 is concerned, it may be testable spectroscopically via expected shifts in vibration frequencies of C=N and NCS vibrations. They should be observed during the lifetime of the oxidized, adsorbed ruthenium complex. Where this type of synergetic bonding is disturbed by deviations from the optimal interface, that is by "surface states", then entropy export or, in other words, temporal stability, should be decreased.

An interesting additional attribute for the self-organized electron transfer would be that, being fundamentally irreversible, it can be calculated to become orders of magnitude

faster than regular electron transfer. Non-equilibrium electron transfer could indeed be described via a non-equilibrium adiabatic mechanism in which a small amount of electronic energy is circulated via a feedback loop. This pushes the system far from equilibrium, where new phenomena are possible. The proposed synergetic mechanism may explain why a change of the back bonding situation, e.g. replacing Ti by Zn would decrease the electron transfer rate and also stability.

Altogether it can be concluded that the problem of sensitizer–substrate interaction remains one of the most critical aspects of sensitization solar cell development. Pushing understanding further may provide the basis for obtaining long-term photo-stable sensitizers.

2.7. Electrolyte instability and electrolyte contamination

As explained before, the iodide/triiodide redox couple has proven to be highly successful in dye sensitization solar cells because of its inherent kinetic irreversibility. Electrons are much more easily donated by iodide than recaptured by triiodide. The suppression of the reverse reaction here is not a phenomenon involving the Marcus inverted region, since replacement of I^-/I_3^- by redox systems with similar redox potentials ($Fe^{2+/3+}$, $Fe(CN)^{3+/4+}$, quinone/hydroquinone) leads to a significant drop of solar cell efficiency. Unfortunately, iodine is known to be photochemically reactive. It can engage in photochemical mechanisms especially by dissociating into atomic iodine, which is a radical and participating in many reactions. It can also photochemically react with oxygen [54] or other redox species [73]. Water is excluded from the electrolyte when using the Ru535 complex in sensitization cells due to its negative effect on bonding to TiO_2. However, sealing techniques for liquid dye sensitization solar cells are far from perfect so that problems arise [74]. Even if the much applied Syrline sealing technique is used, infrared studies show that gradually water molecules diffuse from the atmosphere into the cell. The consequence is a reaction with triiodide leading to iodate with intermediates of the iodine electrochemistry reacting further with oxygen and water [56]. The regeneration of the oxidized sensitizer S^+ by iodide in water- and oxygen-free organic electrolyte (6)

$$2S^+ + 3I^- \rightarrow I_3^- + 2S \quad (6)$$

will, with a certain probability, change in presence of water and oxygen, to Eq. (7):

$$2S^+ + 3I^- + 4O_2 + H_2O \rightarrow 2S + 3IO_3^- + 2H^+ \quad (7)$$

According to the iodine potential–pH diagram, the potential variation for the oxidation of I^- to IO_3^- with pH follows the law: potential $V = 1.085 - 0.0591\,\mathrm{pH}$ [75]. Water and oxygen access therefore leads to a depletion of iodine (triiodide) so that the electrolyte gets bleached. The side reaction occurs at the sensitizer adsorption site where triiodide is generated. Iodate may crystallize there because it is not found in the electrolyte, when IR spectroscopy is applied in situ [56]. Such a degradation of the redox electrolyte is especially frequently observed when the solar cell, containing acetonitrile, is allowed to heat up beyond 55 °C. Some complications with the iodide/triiodide redox couple have been analyzed [76] as well as with electrolytes generally [77]. With approximately 5% efficient solar cells, kept at 45 °C, photocurrent decreases between 10 and 25% were typical for continuous solar simulating illumination during a period of 2 months. The solvent propionitrile appeared to behave better than acetonitrile or methoxypropionitrile, and these much better than methoxyacetonitrile, with which photocurrents dropped to less than 30%. This research initiative assumed the sensitizer to remain stable. This is in contrast with the experience of our research group, which clearly identified light-induced degradation using selective illumination in combination with photocurrent imaging techniques (Figs. 7 and 8) [54–56]. The high viscosity imidazolium iodides, which have yielded cells with 6% efficiency, are promising candidates for high stability cells, but other electrolytes with complementary chemical modifications appear to be equally promising: Grätzel's group succeeded in showing, with 7% efficient dye solar cells containing a methoxypropionitrile electrolyte in conjunction with a surfactant ruthenium complex, that 1000 h of cell operation can be sustained with little degradation at up to 80 °C [25]. This is significant progress, but it is in contradiction to the electrolyte instability studies mentioned above which already saw degradation of methoxypropionitrile-based solar cells at 45 °C during a similar period [77]. Is the better attachment of the Ru complex in Ref. [25] a key to more stability? Progress with temperature stability is essential since a solar light absorbing material behind a glass window (producing a green house effect) may heat to such temperatures, if the radiation and heat balance is not optimized to control heating.

In situ infrared studies have also revealed that something occurs with the lithium ion, which is present in the electrolyte for better cell performance. Lithium induces a splitting of the C–N stretch vibrations [56]. This effect is found to decrease during a prolonged solar cell illumination (23–84 days). This indicates that lithium is moving elsewhere and the most probable mechanism is that lithium gets superficially inserted into TiO_2 forming a surface recombination site there. This will lead to a gradual solid-state modification of the TiO_2. While some of the degradation problems will be reduced by better sealing techniques, which may gradually develop (especially SiO_x-based sealing) other problems can apparently only be avoided by abandoning the liquid electrolyte. Electrolyte degradation is responsible for a frequently observed deterioration of dye sensitization cell function. It is not a photo-degradation but a dark degradation, which will influence photo-degradation, since it will reduce the cell photocurrent due to an increase of the solar cell's internal resistance. The smaller photocurrent will in turn decrease the generation rate of photo-degradation products.

3. Solid dye sensitization solar cells

Since the confinement of aggressive liquids poses major problems and since the solid-state solar cells are easier to handle, there have been many efforts to pass from liquid to polymeric, gel-type and solid electrolytes or contacts [78–85]. This research was also accompanied by the hope that degradation and confinement problems of the electrolyte could thereby be circumvented. This even seemed to justify a lot of effort with quite low efficient prototype cells. A big problem turned out to be the necessary interpenetration of the sensitized oxide and the solid contact material while sustaining a vectorial charge-separating interface. In other words, the suppression of electron reverse reaction from the oxide and the FTO front contact with the irreversibly reacting iodide/triiodide electrolyte in the wet cell has to be accomplished at a highly structured oxide/solid contact interface. This explains why progress with solid-state dye sensitization cells turned out to be painstaking. The best performance was obtained with copper thiocyanate contacts and especially with copper iodide treated with thiocyanate-containing surfactants to obtain fine-grained CuI from an acetonitrile solution. This is desired for better interpenetration of CuI with TiO_2. With the latter cells, photoefficiencies of up to 4% could be demonstrated [81]. However, recent studies on stability in the laboratory of the author showed that this was achieved at the expense of quite dramatic photochemical instability. While wet dye sensitization cells based on the Ru535 complex could survive 2 years (author's experience), solid-state cells using the same dye degraded to 20% within time periods of 60–100 h [86]. Within such short periods, the ruthenium sensitizer should not visibly degrade, especially because it has been bonded to the TiO_2 in the same way as for wet dye sensitization cells. In fact it turned out that the hydrothiocyanate bridge is broken in a photochemical reverse reaction of electrons injected into the TiO_2 structure [87]. The hydrothiocyanate apparently forms a bridge between the sensitizing molecule and the copper iodide. This bridge is photoelectrochemically reduced and interrupted so that the solar cell function degrades rapidly. This again shows that photo-degradation is an important issue, even for solid-state sensitization solar cells. Studies in this field of solar cell stability not only identify problems which have to be solved for long-term operation of the cells, but also indicate essential mechanistic pathways which can be disrupted.

4. Discussion and outlook

This contribution was not intended to be a review of dye sensitization solar cells but was aimed at understanding research progress and progress opportunities. Therefore, it reflects a rather personal view and could consider only selected aspects of dye solar cell research, which were considered critical.

When looking at the learning curve (Fig. 1, bottom) for dye sensitization solar cell efficiency, one realizes that up to 1991, up to the demonstration of high efficient nano-crystalline TiO_2-based sensitization solar cells, the learning curve for laboratory cells is slower than that of crystalline silicon and that found for classical thin layer photovoltaic cells (Fig. 1). This may have been caused by the hesitation of researchers to tackle the problem of photo-degrading organic sensitizers. Progress during this period may basically be explained by progressively exploiting the advantage of large surface area, where more and more sensitizer molecules could be adsorbed for photocurrent generation. While the substrate for sensitization were single crystals and low surface sintered oxide materials they became sintered oxide materials with intentionally increased surface in 1980 [7] before they were fabricated along nano-technological procedures in 1990. The remarkable contribution of the research group around Grätzel is clearly visible (his own view on dye solar cell development is reflected in a recent review [88]). The introduction of Ru complexes, properly bonded to TiO_2, significantly improved the technical quality of dye sensitization cells. After 1991, however, during nearly one and a half decades, and in spite of the participation, worldwide, of approximately 80 groups, some stagnation is observed in the development of solar cell efficiency. This is remarkable especially since the development of short-term efficiency, and not performance stability, became the main target of research. The most efficient standard cells, which could be produced, had an efficiency between 7 and 9% (with a very recent, but again small EPFL cell of 0.158 cm^2 reaching 10.6% [88]). A remarkable fact is that the TiO_2 nano-material, the ruthenium complex and the iodide/triiodine redox electrolyte remained the same. No better alternative materials could be identified. There were, however, significant research efforts aimed at developing alternative electrolyte media ranging from sol–gel to polymeric and molten-salt compounds, aimed at improving the TiO_2 nano-material, and at understanding charge transport dynamics in the nano-environment. In the last area significant progress was achieved [89–91]. It seems that more ordered nano-structure networks provide an advantage [93].

What are the reasons for the comparatively slow path of dye solar cell development, considering that the thermodynamic efficiency limit of a one-absorber quantum converter absorbing up to 800 nm (such as Ru complexes) is in the range of 30%.

The most probable explanation for this stagnation in spite of a quite significant international research effort and progress in understanding is that the research frontier has changed and new problems, which provide obstacles for a further efficiency increase, were not addressed to a sufficient extent.

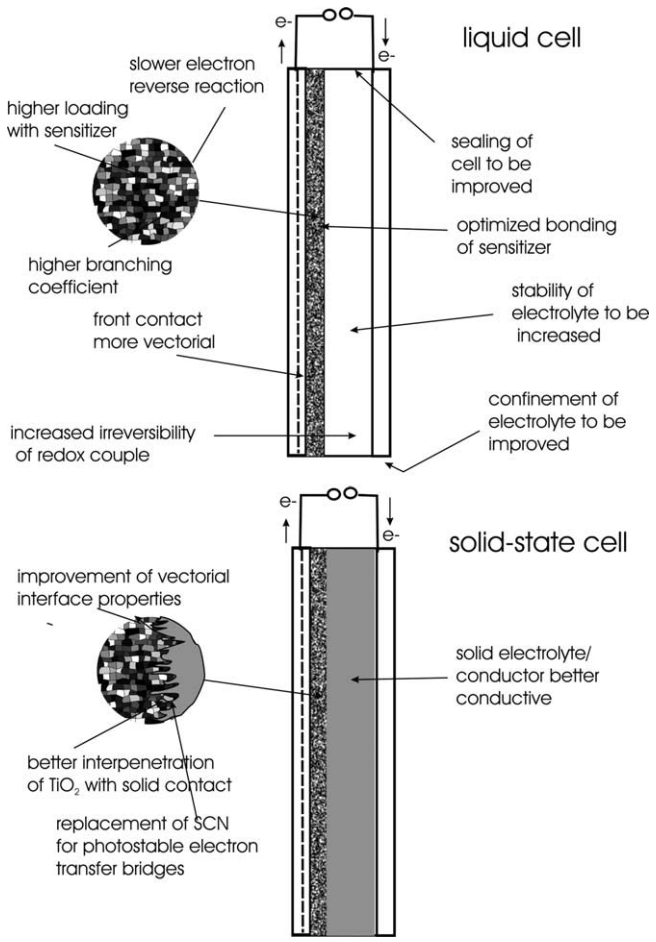

Fig. 11. Scheme explaining key problems of dye sensitization cells, both liquid and solid.

4.1. What are the key challenges?

The main challenge, according to our analysis, is the role of irreversible kinetic charge separation in nano-crystalline environments (Fig. 11). The electrical field, which is responsible for charge separation in classical photovoltaic devices, has been gradually and empirically replaced by an irreversible interfacial kinetics, which does the same job in separating charges but which requires entirely different physical/chemical conditions. This is the same principle which Nature applies in the photosynthetic membrane. It reflects the most simple function mechanism of a solar cell. Electronic charges are only allowed to move in one direction. For dye sensitization solar cells this irreversible kinetics is critical both at the nano-particles as well as at the FTO front contact. By experience it turned out that the iodide/triiodide system is especially favorable for sensitization solar cells. It was contained in the most efficient sensitization cell based on sintered zinc oxide material in 1980 [7] and was part of the high surface area nano-crystalline new cells developed since 1991. The iodide/triiodide system with its significant kinetic irreversibility, with respect to electron transfer, provided the necessary condition to guarantee a reasonably efficient operation of the dye sensitization solar cell according to Fig. 2 (bottom). This irreversibility improved the systems from a purely photogalvanic cell to a well performing solar cell based on vectorial charge separation. However, up to now comparatively little effort has been made to understand and develop the function of kinetic irreversibility and to investigate the fundamental properties of irreversible electron transfer processes. While the classical Marcus–Gerischer approach to electron transfer at interfaces, which is based on reversible statistics and quantum tunneling processes, leaves room for the explanation of irreversible mechanisms via the Marcus inverted region, irreversible thermodynamics and electron transfer involving autocatalysis may offer alternative working tools for developing and understanding irreversible processes of the kind needed for dye sensitization solar cells. In properly tailored molecules and interfaces, which provide autocatalytic mechanisms allowing a small amount of energy to act with the environment in feedback, stimulating or suppressing electron transfer can generate entirely new phenomena. They range from drastically increased rates of electron transfer to cooperative mechanisms and multi-electron transfer. Common to all these phenomena is the irreversibility, giving rise to vectorial interfacial properties, which we consider a key to improve dye sensitization cell properties. This does not only concern the surface of nano-particles, but also the FTO/electrolyte front contact. Comparatively little (published) research has up to now been performed towards increasing the vectorial properties of the latter, for example by co-adsorbing surface-active molecules. There are however interesting recent studies performed on the influence of alkylpyridine additives, which show a significant effect on the photovoltage and the power output characteristic of dye solar cells [24]. The dipole moment as well as the size and ionization energy of pyridines could be correlated with cell parameters. 2-Propylpyridine was found to be more active than the previously used additive 4-*t*-butylpyridine. The above mentioned 10.6% efficient small area solar cell [88] took advantage of the favorable effect of guanidinium thiocyanate, which adsorbed to the sensitized interface thus improving the cell voltage.

The second most important challenge is that of sensitizer stability. Transition metal complexes are better suited than purely organic dye molecules. The reason obviously is that they allow metal-centered electron transfer, which is more specific and avoids side reactions. This appears to be a necessary but not sufficient condition for stability because the way of attachment to the oxide substrate is most critical. The same sensitizer in homogeneous solution or weakly adsorbed to an oxide can be photochemically very reactive and unstable while it may become highly stable when properly attached to the oxide. The fact that the state of adsorption and interaction of the sensitizer with the oxide is influencing its stability has been known since the early time of sensitization research [3] and has been reconfirmed by recent research in our group. The sometimes observed significant variation in sensitizer stability within an individual cell and

the dependence of sensitizer stability on pre-treatment of TiO_2 can only be explained if surface states are involved. This also explains why photo-induced degradation is sometimes quite significant at the beginning of illumination of a sensitization solar cell. Those sensitizer molecules, which are unfavorably attached to the TiO_2 then rapidly degrade while the long-term stable adsorbed sensitizer molecules will survive. Research is therefore necessary to understand the surface chemistry of the dye–oxide interaction. Improved stability requires optimized adsorption sites, which can only be identified through systematic research.

In addition the long-term stability of entire sealed solar cells under operation conditions (50–80 °C) in intense sunlight has to be better addressed. Here, a significant contribution has recently been provided by Grätzel's group, where a modified Ru sensitizer complex was used in combination with a quasi-solid-state polymer gel electrolyte to yield 7% efficient cells which well supported heat stress (applied during 1000 h) [26] which the cells have to sustain under outdoor conditions. However, the general problem of temperature effects on the efficiency of dye solar cells has only been addressed recently in a more systematic way [92]. A 30% power output decrease was observed when increasing the temperature from 30 to 80 °C (compare however the contradicting results from Ref. [53], Fig. 1, and Ref. [88]). Mechanisms aimed at limiting the heating effect in solar cells under illumination have to be developed.

Another factor, which determines long-term dye stability is the so-called branching coefficient, the ratio of regeneration rate of the oxidized sensitizer times the iodide concentration divided by the rate for the product formation. Both rate constants may depend on surface chemical parameters and will have to be optimized by studying co-adsorbed molecules, alternative electrolytes and redesigned sensitizers. Since the formation of the oxidized sensitizer molecule and its regeneration may depend on surface state chemistry, this aspect is quite complicated and will need special attention.

It was also pointed out that, surprisingly, solid-state sensitization solar cells based on copper iodide hole conduction showed a much higher photo-degradation than liquid dye sensitization solar cells [68,69]. It turned out that the necessary additive, a hydrothiocyanate-containing molecule used for conditioning the CuI into the TiO_2 nano-structure, also played a second role. It provided an electronic bridge for the regeneration of the ruthenium sensitizer and is apparently destroyed through a photoelectrochemical reverse reaction of electrons into TiO_2. This shows that photochemical stability will also be a central problem for solid-state dye sensitization solar cells. Research is needed to identify stable pathways for charge separation.

It is to be hoped that when the relevant scientific questions are asked, faster progress towards the realization of stable and efficient dye sensitization solar cells can be accomplished. In the past, this has not always been the case. Besides empirically co-adsorbing molecules essentially no systematic research has been performed on how to improve vectorial, irreversible interfacial processes, in the absence of electrical fields, to further reduce reverse reactions of electrons. Photo-degradation studies to evaluate long-term performance have also been long neglected. They did not fit the image of a successful new solar cell. The author, in fact, heard the argument that funding agencies would not easily be willing to support research on a cell with major stability problems. Remarkable is also the research community's attitude in the case of solid-state sensitization cells. For years research in this field has been justified, and the quite small solar cell efficiencies accepted, because of the expectation that solid-state cells can avoid all disadvantages and instabilities of wet sensitization solar cells. When photo-degradation studies on solid-state cells were started in the author's laboratory in 2003, the expectation was that these cells should be much more stable than the wet ones. In fact it turned out that they were 100 times more unstable. How could such a negative property have escaped wider scientific attention before? Or was it simply ignored because the search for higher efficiencies was considered more rewarding? A healthy balance has to be found between necessary research tasks and rewarding research challenges to secure a longer-term interest of funding agencies in the field of innovative energy research.

This critical analysis of the learning curve for dye sensitization solar cell efficiency has pinpointed probable reasons for its temporal difficulties. Also the problem of limited lifetime, which is a key cost factor for solar cells, has been insufficiently considered and evaluated. One also has to address the learning curve for cost efficiency more aggressively. On the other hand it is a positive investment for the future, when so many interesting studies are made on the most diverse aspects of dye sensitization solar cell function. It is therefore hoped that, after some time for reflection and reorientation, the learning curve for dye solar cell efficiency will speed up again.

What will their future be? When considering the large number of parameters affecting the quality and long-term stability of dye solar cells, our feeling is that its development will be somehow comparable to the experience of photography. Over a long period photography mostly developed empirically with many small discoveries being incorporated into the technology. In this way the quality of photography gradually improved while being commercialized. Only later scientific research started to understand detailed molecular processes and to control progress. The difference today is that advanced research capabilities have made progress to proceed much faster. By asking the right questions nano-crystalline dye sensitization solar cells could be developed more efficiently towards urgently needed applications as affordable solar energy devices. This contribution was an attempt to stimulate new discussion, but also to stimulate comments of other researchers on bottlenecks for dye solar cell development.

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