Are dye-sensitized nano-structured solar cells stable?
An overview of device testing and component analyses

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ABSTRACT. The nano-structured dye-sensitized solar cell (DNSC) is considered as a promising technology having the potential to significantly decrease the costs of solar energy. The breakthrough was achieved in 1991 with the demonstration of a DNSC system reaching more than 7% efficiency and after a decade of intense research the commercialization is in reach. Besides efficiency, stability is equally important for the step from research to the market. Therefore, the stability of such devices has been under close investigation since the DNSC was presented. In this contribution we summarize the literature about device testing and the attempts to understand the degradation mechanisms. Solar cells developed for energy production are discussed as well as alternative systems for low power applications, e.g., DNSCs on plastic substrates. The components (substrate, nano-structured TiO_2, dye, electrolyte, additive and counter electrode) are analyzed towards their stability and how it affects the durability of the entire system. From this analysis, guidelines for testing and improving the stability of the DNSC are deduced.

1. INTRODUCTION

The product of efficiency and stability determines the value of every device converting light energy into electricity. This applies for "traditional" silicon solar cells as well as for innovative devices like the dye-sensitized nano-structured solar cell (DNSC). The photoelectrochemical cell is a typical example of an integrated chemical system (ICS) and has been under investigation for a few decades [1–3]. Nevertheless, the low performance in terms of efficiency or stability has prevented this type of solar cell to become a commercial success. In 1991, O'Regan and Grätzel presented a photoelectrochemical system, which promised for the first time a combination of competitive efficiency (between 8% and 10%) in combination with a promising stability. This was achieved by introducing nano-structured TiO_2 electrodes in combination with Ru-based dyes, which inject electrons into the conduction band of the semiconductor under illumination. A redox couple that itself is reduced at the counter-electrode regenerates the oxidized dye (Figure 1) [4]. Though the concept of dye-sensitized solar cells has been presented before, the nano-structured material provided for the first time the required area for sufficient light absorption. Since only a monolayer of dye is adsorbed, a flat surface is not able to harvest enough light to deliver reasonable light-to-energy conversion efficiencies.

The breakthrough with the introduction of the DNSC system is indeed remarkable: For the first time a molecular system was presented in which the thermodynamics as well as the kinetics are so well balanced that a considerable light-to-energy conversion efficiency was achieved. Also, this fine balance seems to sustain the high efficiency for a significant time. From this viewpoint, the system can be described as a molecular machine in which photo excitation and directed mass and energy transport works in a similar fashion as in natural photosynthesis. Therefore it can be described as an artificial photosynthetic machine producing electrical energy instead of chemical energy.

Whereas the durability of the well established single-crystalline and amorphous silicon modules is not questioned for a life-time of 10 to 20 years, newly emerging techniques like the DNSC are still under close observation to determine whether they are able to deliver a stable performance for at least 10 years under working conditions. These concerns stem from the complicated and well balanced interplay of the large number of components [4]. Since the first presentation of a dye-sensitized photoelectrochemical cell including nano-structured TiO_2, the stability has been intensively discussed and a number of controversial contributions have been published. These efforts can be divided into investigations dealing with the testing of complete devices on one side and the analysis of components on the other. The structure of our contribution reflects this division: In the first part we describe the attempts to test cells and modules in long-term and accelerated tests. In the second chapter, we will try to give an overview of degradation mechanisms component by component. A summary of processes which have been investigated and published is presented. We also give as suggestions for cell failure mechanisms, which have not been observed or described in the literature yet, but could play a role in long term operations of DNSCs. In terms of quality control in a production process it will be important to develop a detailed understanding of all possible mechanisms to be able to identify where in the process the failure occurred. In the last part of our discussion,
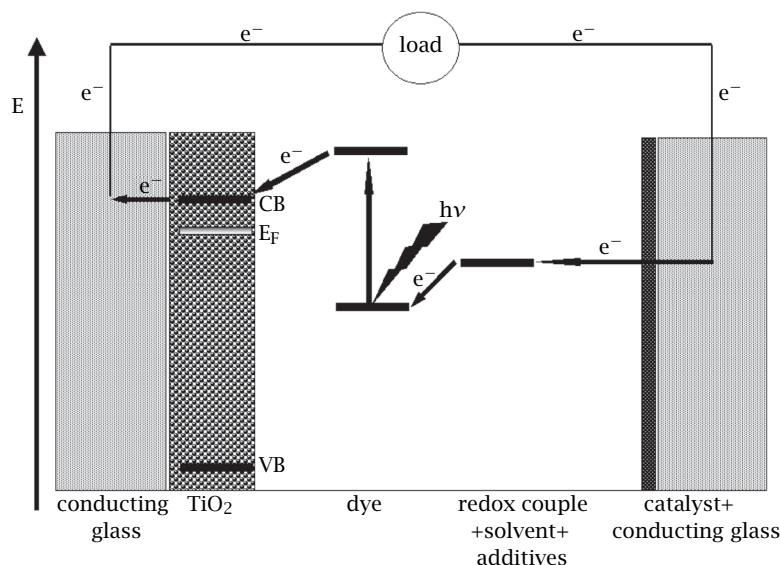
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Figure 1. *Working principle of the DNSC (VB: Valence band; CB: Conduction Band; E_F: Fermi level).*

we will try to give some guidelines for testing DNSCs in order to make prediction of lifetimes and we also conclude what measures have to be taken in order to achieve a maximum of stability.

2. DEGRADATION MECHANISMS—DEVICE TESTING

2.1. High-power devices.   With the publication of an efficient dye-sensitized photoelectrochemical solar cell based on nano-structured TiO_2 by O'Regan and Grätzel in 1991, researchers and engineers started to explore the possibilities of using this kind of cell commercially. Naturally, the lifetime of these cells became an important issue. In the following decade, stability data was published together with light-to-energy conversion efficiencies in a number of papers presenting alternative components. Moreover, studies were published dealing exclusively with issues concerning stability.

A comparison of these investigations is difficult because the cell's construction as well as the used components vary to a large extent. In the following we summarize the results dealing with the degradation of cells with designs similar to the one published by Grätzel and O'Regan in 1991 [4]. These cells consist of nano-structured TiO_2 converted into an electrode by sintering a suspension onto a sheet of glass with a layer of conductive material, a ruthenium complex as the photoactive component, I^-/I_3^- as the redox couple and an organic solvent–usually a nitrile derivative. The counter-electrode consists in most cases of a platinized glass electrode. Alternatively, carbon was used instead of platinum in order to provide a large surface area for a sufficient reduction of the redox couple.

Already in 1991 O'Regan and Grätzel discussed the stability and mentioned that they monitored cells for periods up to 2 months. The cells lost less than 10% of the initial photocurrent [4]. The system under investigation was built of sintered nano-structured TiO_2 dye sensitized with $Ru(II)(bpca)\{(\mu\text{-}CN)Ru(II)(CN)(2,2'\text{-}bipyridine)_2\}_2$ (bpca = 2,2'-bipyridyl-4,4'-dicarboxylic acid). The electrolyte used was a mixture of ethylene carbonate and acetonitrile in conjunction with tetrapropylammonium iodide and diiodine. In the following years degradation processes were rarely discussed in the scientific literature. When Nazeeruddin et al. introduced the *cis*-$(SCN)_2(bpca)_2Ru(II)$ chromophore ("Red Dye") as dye sensitizer, performance as a function of time was published in order to demonstrate the extraordinary stability of the system [5]. The authors reported that a continuous illumination of cells for a period of 10 months the cells showed a decrease of the photocurrent by only 20 to 30%. It was also mentioned that a careful filtering of UV-light stabilizes the cells. 3-Methoxy-2-oxazolidone in combination with LiI/LiI_3 served as the electrolyte.

The first publication known to the authors exclusively dedicated to long term stability tests of DNSC was presented by Kay and Grätzel in 1996 [6]. They monitored the evolution of the short-circuit current (I_{SC}) and open-circuit voltage (U_{OC}) as a function of time over 110 days for cells built in a monolithic design, which incorporated nano-structured TiO_2 material as the working electrode, *cis*-$(SCN)_2(bpca)_2Ru(II)$ as the dye, a carbon counter electrode and a solution of $1\,M$ tetra-butylammoniumiodide/$0.1\,M$ I_2 in acetonitrile as the electrolyte. Tetra-butylammonium-hydroxide and 4-*tert*-butylpyridine, respectively, were added to the electrolyte as well. The cells were stable with respect

to the overall efficiency at a light intensity of $800\,W/m^2$ for the time of evaluation. Nevertheless, a decline of the photovoltage was observed, which was compensated by an increase in photocurrent. Following this study, Grün-wald and Tributsch published a contribution dealing with the degradation of the DNSC [7]. It was reported that the cells under investigation degraded rapidly due to leakage of the cell electrolyte and the attention was drawn to the general problem with the sealing of the cell. Also, the degradation of the Ru-dyes in operating DNSCs was investigated by means of in-situ infrared spectroscopy. Under the impression of their results the authors questioned the data published before [4, 5]. Shortly after this challenge of the stability, Kohle et al. presented a study in which cells showed no decrease in performance over a period of 7000 hours of continuous illumination at AM 1.5 and $35\,°C$ [8]. Degradation was only observed when the cells were kept at elevated temperatures ($75\,°C$). Moreover, the time of 7000 hours of stability was extrapolated to 6 years under working outdoor conditions in Central Europe. The cells under investigation consisted of nano-crystalline TiO_2 sensitized with cis-Ru(bpca)$_2$(SCN)$_2$ and an electrolyte with glutaronitrile as the solvent and $0.5\,M$ KI/$50\,mM$ I$_2$ as the redox couple. It should also be mentioned that a $395\,nm$ UV cut-off filter was used.

The issue of stability of the DNSC was picked up by a group of institutes (ECN, The Netherlands; Freiburg Materials Research Center, Germany; Institut für Angewandte Photovoltaik, Germany and Solaronix S.A., Switzerland) trying to systematically investigate the long term behavior of DNSC modules. This consortium has published three major studies so far, which can be summarized as follows: [9–11].

In 1998 the authors tested a variety of cells under light intensities 2 to 3 times higher than the solar radiation as well as in outdoor set-ups [11]. All cells investigated consisted of nano-structured TiO_2 on conducting glass sensitized with cis-Ru(bpca)$_2$(SCN)$_2$ and an electrolyte solution of methoxypropionitrile with $0.5\,M$ LiI and $0.05\,M$ I$_2$. Beside these basic components, the additive 4-*tert*-butylpyridine was added to some cells in combination with water and without water in order to test the influence of this compound on the degradation behavior. The cells sealed with Syrlin® were tested over a period of about 2000 to 3000 hours. This preliminary investigation was followed up by a publication of stability data in the year 2000 [10]. Using similar components as in the earlier study, the degradation was investigated at high light intensities (2.5 times the sun equivalent intensity) towards the influence of 4-*tert*-butylpyridine and the solvent. This investigation confirmed the positive influence of the additive towards water sensitivity and stressed the fact that the electrolyte solvent has a significant effect on the stability. It could be shown that propionitrile is the best solvent with respect to the durability. Cells working with other nitrile solvents–

in particular acetonitrile and methoxyacetonitrile - degraded faster.

The last study published by the consortium appeared in 2001, in which they covered the testing of the influence of high light intensities, UV-light exposure and increased temperatures. The devices consisted of the same basic components (cis-Ru(bpca)$_2$(SCN)$_2$, $0.5\,M$ LiI and $0.05\,M$ I$_2$) as before, but also the influence of a number of additives and solvents on the stability was investigated in more details. The results can be summarized as follows: At $45\,°C$ and 1 sun light intensity good stability over a period of 3400 hours was achieved with propionitrile as the solvent (loss of efficiency smaller than 15%), whereas cells with methoxy-acetonitrile were degrading at a much faster rate. MgI and CaI showed a strongly stabilizing effect when the cells were exposed to UV-light. Cells were also tested at elevated temperatures. It turned out that at $85\,°C$ the best cells lost less than 30% of efficiency within 875 hours.

The latest study known to the authors was performed and published by Wang et al. [12]. Two main components were altered with respect to the preceding DNSCs: The dye and the electrolyte. The usually applied cis-Ru(bpca)$_2$(SCN)$_2$ was modified by replacing one of the bpca ligands by the amphiphilic ligand 4,4'-dinonyl-2,2'-bipyridine and the electrolyte consisted of 3-methoxypropionitrile, which was mixed with a fluorine polymer to give a quasi-solid-state gel-electrolyte. The presented stability data showed a remarkable resistance of the cells towards temperature and light irradiation. A decrease below 5% was observed for cells within a period of 1000 hours at $85\,°C$ as well as for cells stored at $55\,°C$ and 1 sun light intensity. The authors point out that in particular the stability at elevated temperatures is better than for any other DNSCs published so far, because of the stabilizing effect of the hydrophobic ligand and the gelation of the organic solvent. It should be mentioned at this point that Kubo et al. had presented and discussed the stabilizing effect of gelators before [13–15].

2.2. Low-power devices. All the investigations summarized so far have been studying, if the DNSC, as it was published in 1991, has the potential to be stable in long-term outdoor conditions for the use in energy production. In recent years, a few other studies were presented in which DNSCs for low-power applications were published. Cells with innovative concepts have also been tested towards stability, but these cells have low efficiencies and are therefore difficult to compare in terms of performance to the cells described before.

Pettersson et al. presented a DNSC of monolithic design, which incorporated 1-methyl-3-hexyl-imidazolium as the solvent for the electrolyte [16]. These cells show a saturation of the current with
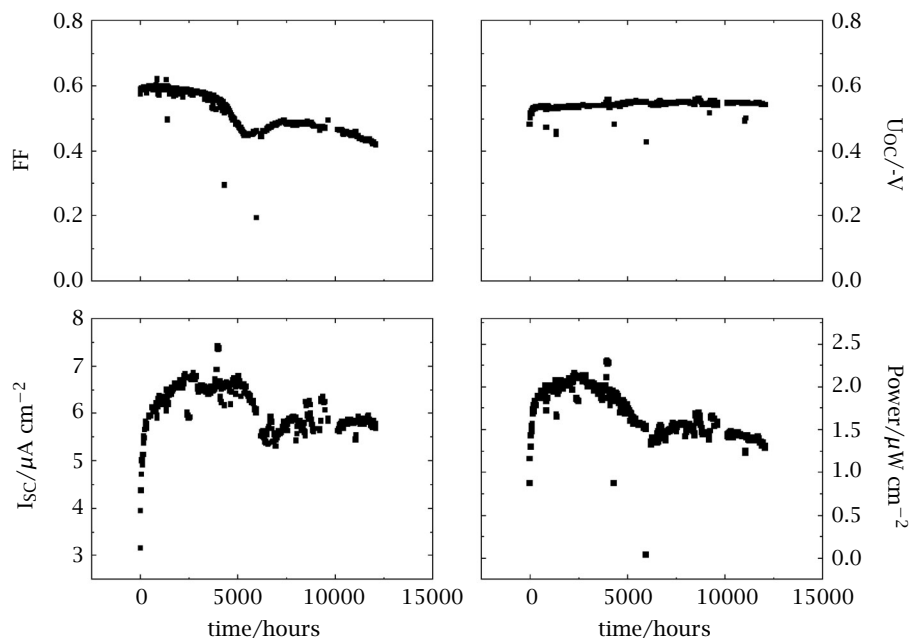
Figure 2. *Performance as a function of time for a DNSC on PET substrate (light intensity:* 250 *Lux; DNSC: cis-*Ru(bpca)$_2$(SCN)$_2$, 0.5 M NaI, 0.05 M I$_2$, 1*-methylbenzimidazole in polyethylene glycol (PEG200)).*

increasing light intensity at 4000 Lux, but exhibit an improved stability. In the same study, the DNSCs were tested towards humidity, UV-light and light. It could be shown that the cells were not influenced by a high humidity in the atmosphere, whereas the cells degraded under UV-light irradiation, which could be suppressed to a large extent by a UV-filter. The influence of light on the stability was tested at 250 Lux, which corresponds to indoor light conditions. Using fluorescent light, the cells were stable for a period of 180 days and it was also confirmed that UV light must be blocked in order to guarantee the durability. An increased degradation was observed at higher light intensities, i.e., at light intensities beyond the linear section of the function of current vs. light intensity. This effect is particularly strong under open-circuit conditions. The authors explain it by side reactions triggered by high charge carrier concentrations. This study was followed-up by another investigation in which the stability data was updated and additional information about the resistance of the cells towards temperature was given [17]. The cells showed an accelerated degradation at temperatures above 50 °C. A few groups have during the last years presented DNSCs in which a flexible plastic substrate substitutes the glass substrate. Sommeling et al. discussed the production and stability of DNSCs on PET substrates [18]. The nano-structured TiO$_2$ electrodes were produced by sintering at rather low temperatures because of the temperature restrictions set by the polymer substrate. The authors reported that the stability

of these cells was rather limited when used to power watches or calculators. Independent tests on the other side revealed promising results with stabilities of a few hundred up to 2000 hours at continuous illumination, when a UV filter was applied to the system. A similar system was presented by Longo et al. [41]: The DNSCs achieved by low-temperature sintering and filled with a polymer electrolyte containing the diiodine-iodide redox couple were tested towards long term stability under continuous 10 mW cm^{-2} light illumination: The efficiency decreased by more than 50% within 50 days. This result was complemented by impedance spectroscopy studies and it was revealed that the series resistance of the cell increases with time under illumination.

We assembled in our laboratories DNSCs on PET substrates. The nano-structured films of TiO$_2$ were produced by the application of pressure [19]. The counter-electrode consisted of pressed platinized SnO$_2$ powder and the cells were sealed with a Syrlin® hot melt foil. As the electrolyte 0.5 M NaI/0.05 M I$_2$ dissolved in polyethylene glycol (PEG200) was applied together with 1-methylbenzimidazole as an additive. Cells with this configuration were tested under indoor conditions (250 Lux, fluorescent light, 30 °C, UV-filter) [20]. The results are plotted in Figure 2 and can be summarized as follows: Up to approximately 5000 hours, no decrease in the power output occurs. Later, a decrease occurs, which is mainly related to a loss in fill factor (FF) and short-circuit current (I$_{SC}$). The voltage on the other side is maintained over the whole period of time (almost

Substrate	TiO$_2$	Dye	Electrolyte	Catalyst	Substrate

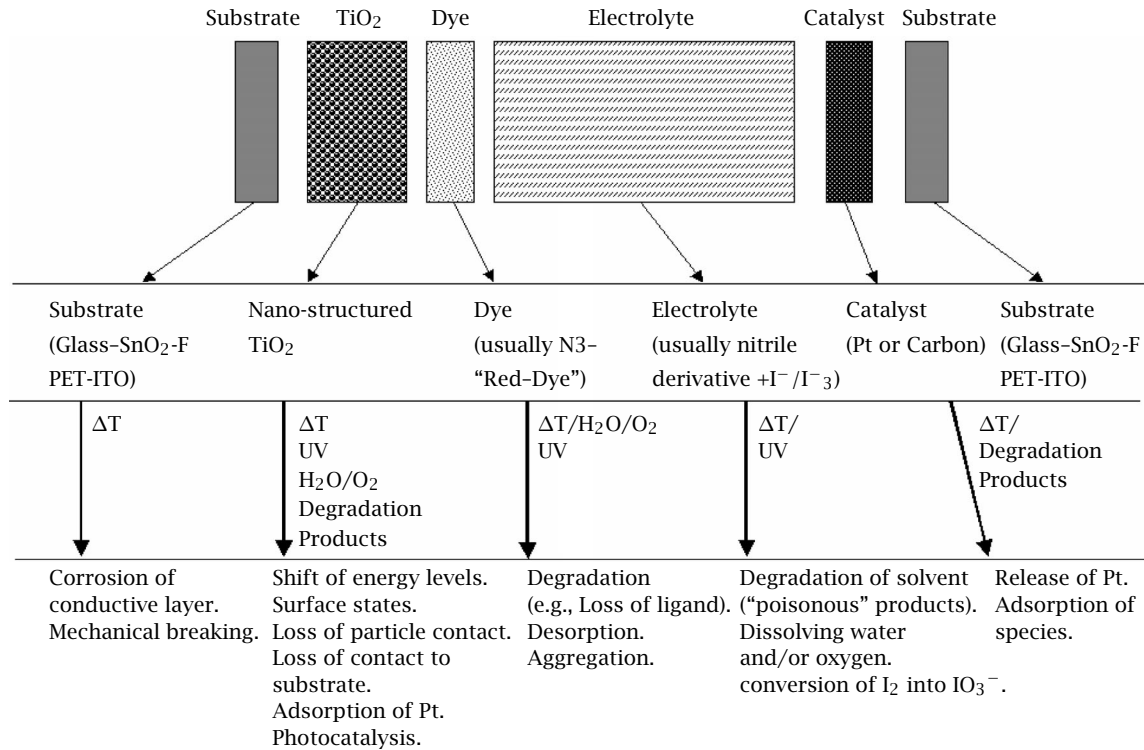| Substrate (Glass–SnO$_2$-F PET-ITO)	Nano-structured TiO$_2$	Dye (usually N3– "Red-Dye")	Electrolyte (usually nitrile derivative $+ I^-/I^-_3$)	Catalyst (Pt or Carbon)	Substrate (Glass–SnO$_2$-F PET-ITO)
ΔT	ΔT UV H$_2$O/O$_2$ Degradation Products	ΔT/H$_2$O/O$_2$ UV	ΔT/ UV		ΔT/ Degradation Products
Corrosion of conductive layer. Mechanical breaking.	Shift of energy levels. Surface states. Loss of particle contact. Loss of contact to substrate. Adsorption of Pt. Photocatalysis.	Degradation (e.g., Loss of ligand). Desorption. Aggregation.	Degradation of solvent ("poisonous" products). Dissolving water and/or oxygen. conversion of I$_2$ into IO$_3^-$.		Release of Pt. Adsorption of species.

Figure 3. *Degradation mechanisms of the DNSC - component analysis.*

1.5 years at continuous illumination). These results are somewhat surprising, since a PET substrate is a poor barrier for oxygen, water and other pollutants.

3. DEGRADATION MECHANISM—COMPONENT ANALYSES

In the following we will give a summary of possible degradation processes of the individual components. An overview of the components, the stress factors and the degradation processes is given in Figure 3. As mentioned in the introduction, the reaction mechanisms discussed are partly hypothetical and it is not always clear, if they apply in the system under working conditions. Therefore the following discussion should be taken as a guideline for failure analysis rather than a description of inevitable events.

3.1. Substrate and sealing. The technical aspects of the substrate and the sealing cannot be sufficiently covered in this contribution since they are rarely published. Therefore only general aspects for the improvement of the durability can be given. Nevertheless, the information given will be of importance for developing techniques and know-how around failure analyses of cells under operation, for quality control in a production process, etc..

The encapsulation of the cells should prevent the exchange of material between the cell and the environment: First of all, the sealing must prevent evaporation of the electrolyte solvent, but it also should be a barrier for I$_2$, which is still present in small amounts. I$_2$ is mainly converted to I$_3^-$ due to the addition of iodide according to the equilibrium $I_2 + I^- \leftrightarrow I_3^-$. Moreover, it should not be forgotten that the regularly applied additive 4-*tert*-butylpyridine has also a significant vapor pressure.

It is also absolutely crucial for the function of the DNSC to stop pollutants from entering the cell. In particular, water and oxygen have a profound influence on the performance as depicted in Figure 3 and described in the following sections.

Closely connected to the sealing of the DNSC is the substrate itself. A number of events can lead to its failure: A mechanical breaking needs to be considered as well as other possible damages to the conductive layer, with the consequence of an increased series resistance in the cell. In this context, a report was published documenting a failure of tin-doped indium oxide (ITO) when voltages above 1.5 V were applied, a potential, which is realistic in solar cell modules [21]. Mechanical breaking can have a number of causes: Most obviously are e.g., hale or storm when the solar cells are used in outdoor installations for energy production. Less obvious is a
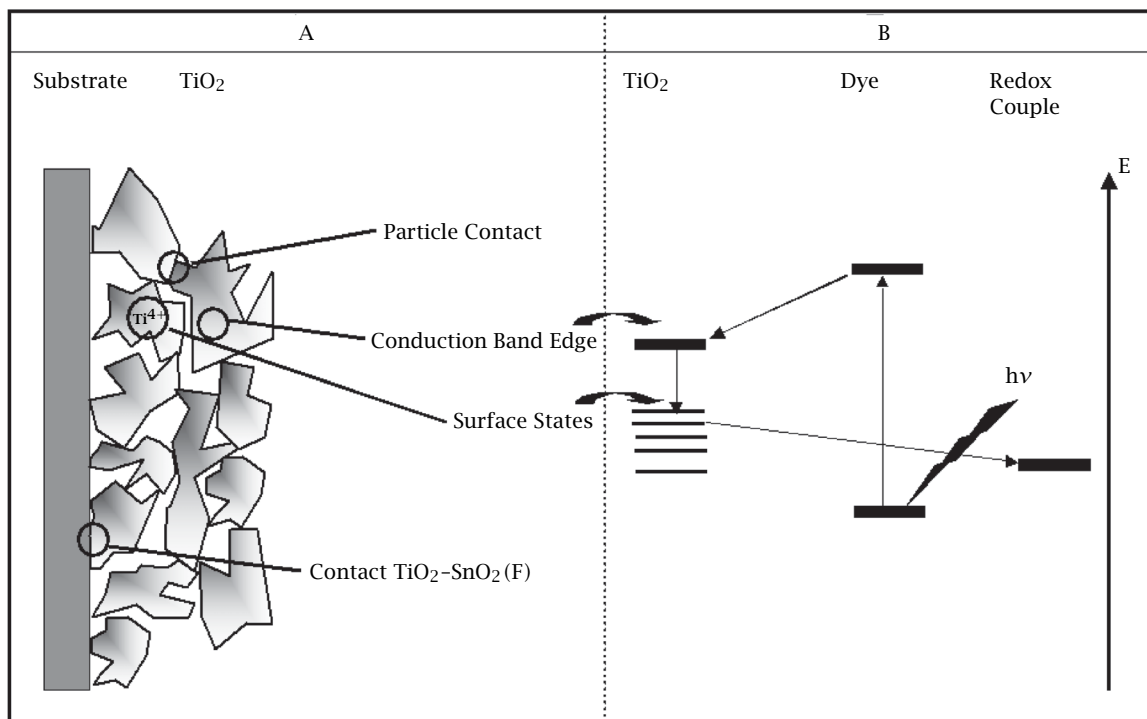
Figure 4. *Points of failure of nano-structured* TiO_2 *(A). Energy diagram of DNSC including surface states (B).*

breaking due to internal processes. We have seen in our laboratories that gas bubbles can break the cell from inside when water has entered the cell. Presumably evolving oxygen and/or hydrogen is the cause of the bubbles. In this respect, plastic substrates are beneficial since gas can diffuse out of the cell without damaging it. The flexibility will also prevent a mechanical breaking. An aspect connected to the substrate and sealing is also the separation of cells in modules. To our knowledge, nothing is reported in the literature about this particular problem so far. The demand of high efficiencies will force the development of very small separation distances between the cells in order to maximize the active area. Naturally, it will be more and more difficult to ensure an electrical insulation of adjacent cells, which is necessary to maintain the photovoltage.

3.2. TiO_2. With respect to the performance of the DNSC, the properties of the nano-structured TiO_2 are crucial. In order to keep the efficiency constant over time, one has to assure that the Fermi level does not shift relative to the dye and the redox electrolyte. Moreover, surface states, which trigger a drain of charge from the conduction band by electron trapping, [22] must be avoided. A loss of electrical contact between the TiO_2 particles could also lead the performance to suffer. These hypothetical points of failure are illustrated in Figure 4(A).

3.2.1   Fermi level

The level of the conduction band edge has a very well defined energy interval in which the cell works most efficiently: If it decreases, U_{OC} drops because of the reduced potential difference between the Fermi level and the level of the redox couple. On the other side, if the energy increases, the injection of electrons from the excited state of the dye might be less efficient, resulting in a decreased I_{SC}. The position of the conduction band edge is determined by the surface charge. Protons in the electrolyte solution for example will adsorb onto the surface and therefore shift the Fermi level and influence U_{OC}. The concentration of protons in the electrolyte may change due to the penetration of water into the cell leading for example to an increased number of protons and therefore to a lower Fermi level resulting into a lower U_{OC} [23]. It seems reasonable that the addition of pyridine derivatives as bases can counteract this effect by buffering protons. Indeed, a stabilizing effect of 4-*tert*-butylpyridine was found when water was added to the cell on purpose [11]. It is also possible that pyridine adsorbs onto the surface and prevents adsorption of species responsible for any conduction band shift. Another way to stabilize the conduction band edge might be to modify the surface with an insulating layer like Al_2O_3 as it was e.g., described by Kay and Palomares et al. [24, 25]. Alternatively, surface
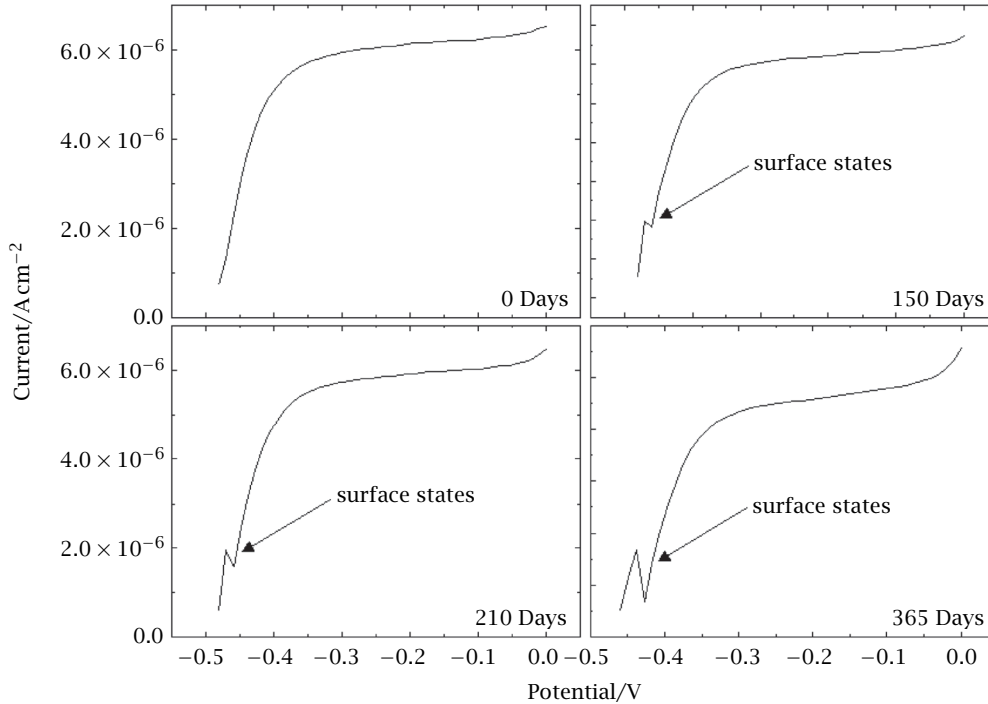
Figure 5. *Evolution of IV-plots as a function of time for DNSCs (light intensity:* 250 *Lux; DNSC: cis-*Ru(bpca)$_2$(SCN)$_2$, 0.5 M NaI, 0.05 M I$_2$, 1-*methylbenzimidazole in polymeric solvent).*

contamination leading to a band shift can be prevented by carboxylic acids [26]. The authors report that such groups co-adsorbed with the dye prevent I$_3$⁻ from adsorbing to the surface, which would increase the back-electron transfer with a loss of performance as a result.

3.2.2   Surface states

An alternative degradation mechanism involves surface states, i.e., energy states below the conduction band (Ti^{4+} ions at the surface of the TiO$_2$ particles—Figure 4 (B)) [27]. It has been discussed that the electron transfer from the conduction band of the TiO$_2$ to the electrolyte takes place mainly through these states [28, 29]. Though it has not been reported in the literature yet that such defects evolve with time, we observed an increase of a peak in the current-voltage characteristics measured at indoor light conditions (250 Lux) (Figure 5) for DNSCs on plastic substrates investigated for longer periods of time (see also Figure 2) [20]. It can be assumed that this peak is caused by the development of surface states, since the position of the peak coincides remarkably well with the potential of surface states determined by cyclic voltammetry [30]. Of course, one has to consider that the plastic substrate is permeable for oxygen and water. Also, the TiO$_2$ films were pressed in order to gain electrical contact between the particles, which certainly makes them different to the sintered films used usually in DNSCs [19]. Nevertheless, it shows

that the development of surface states with time is possible and therefore needs to be considered.

In this context the general photocatalytic properties of TiO$_2$ should be mentioned since it could trigger the decomposition of the components in contact with the TiO$_2$ surface (electrolyte, dye, solvent). For example, in the presence of oxygen and water, hydrogen peroxide can be formed, which itself can destructively oxidize organic compounds [31–33]. The production of H$_2$O$_2$ is initiated by the reduction of O$_2$ by conduction band electrons, followed by a reaction of O$_2$* with H$_2$O. It can be speculated that the oxygen radical itself can directly oxidize organic components of the cell. Therefore the destructive property of oxygen appears already without water. This assumption is supported by investigations of dye degradation mechanisms [34].

3.2.3   Electrical contact

A possible increase in the electrical resistance within the nano-structured TiO$_2$ with time is a factor, which so far has not received much attention in the literature. This resistance is a function of the contact between the particles and the substrate and between the particles themselves [35]. It can be assumed that this problem is small for sintered films, because the sintering process assures an equilibrated system at operating temperatures. On the other side, nano-structured electrodes produced at moderate temperatures by

sol-gel processes or compression might undergo re-cristallisation processes, leading to, both, a changed particle contact and a change of the interface between the conducting substrate and the TiO_2 material. That the latter process can have an influence on the performance was recently shown by impedance spectroscopic analyses of the interface between SnO_2:F and the TiO_2 particles [36].

3.3. Electrolyte

3.3.1 Redox couple

A few authors have reported a bleaching of the redox electrolyte consisting of I^-/I^-_3 at high light intensities, which was assigned to a photodecomposition of diiodine [9, 37]. A loss of I_2 would trigger a decreased recovering rate of the oxidized dye leading to a degradation of the dye with time. Moreover, the internal resistance would increase, which is accompanied by a drop in fill-factor. The authors suspect an oxidation of the diiodine to iodate (IO^-_3) due to UV illumination or oxidative surface states, similar to the already mentioned photocatalytic processes at the TiO_2 surface. It can be speculated that the radical species I_2^{*-} plays an important role in this process [38]. Acceleration of such a degradation due to temperature and traces of water was mentioned as well. A direct detection of IO^-_3 by infrared spectroscopy has not been successful yet [37].

3.3.2 Solvent

The electrolyte solvent has a major impact on the stability of the DNSC. Of course, one has to distinguish between durability problems related to evaporation on one side and destructive mechanisms due to chemical degradation on the other. In this contribution we cannot discuss the evaporation problem in detail since, as mentioned before, sealing techniques are rarely presented in the literature. Nevertheless, it should be noticed that many attempts to decrease the solvent evaporation rate by the use of gelators in combination with organic solvents as well as molten salts and polymeric solvents have been published [12–15, 39–41]. These approaches still include the I^-/I^-_3 redox couple as charge carrier, whereas modified DNSC designs with organic and inorganic hole conductors have been presented in order to entirely substitute organic solvents [42–50]. Chemical degradation of the solvent has been—as mentioned before—already discussed by Hinsch et al. and Kern et al. [9, 10]. The main result of these studies was that pure nitrile-based solvents are superior to oxygen containing ones like 3-methoxypropionitrile (3-MPN). It was suggested that traces of water trigger hydrolysis reactions leading to methoxyacetamide in the case of 3-MPN, which was detected as a degradation product. Nevertheless, it is unclear how degradation products will influence the solar cell performance. An adsorption

to the catalyst surface of the counter electrode is possible, which would lead to a reduced reduction rate of the redox couple, but also an adsorption onto the TiO_2 surface with unpredictable consequences is possible.

3.4. Counter electrode.
Using a platinized counter electrode, 4 processes can be identified leading to a loss of performance over time:

1. Release of Pt from the counter electrode: Pt atoms and fragments of Pt clusters diffuse to the working electrode, adsorb onto the SnO_2: F and lead to an increased back electron transfer with the consequence of a reduced I_{SC} [9].

2. Pt released from the counter electrode can adsorb onto the TiO_2 surface changing its photo-electrochemical properties [51–53].

3. Release of Pt leads to a loss of the catalytic properties of the counter electrode, with the result of a decreased recovery of the oxidized iodine redox couple. A reduced FF and I_{SC} would be the consequence of this process.

4. Degradation products from the electrolyte might adsorb onto the Pt surface, blocking the catalytic activity with the same result as described before.

The adsorption of small amounts of Pt onto the TiO_2 can effect its electrical and catalytic properties profoundly [51–53]. Already in the early 80's, it was described that Pt on the TiO_2 can trap electrons and reduce the photoconductivity of the material. Consequently, this would lead to a lower fill-factor due to the higher resistance in the nano-structured TiO_2 as well as an increased recombination rate with the oxidized iodide in the electrolyte. Another mechanism of instability is a consequence of the trapping of electrons by the Pt: The excitation of valence band electrons by UV-light generates holes having an increased lifetime due to the trapping of the electrons, which leads to the improved photocatalytic properties of Pt-doped TiO_2 [54]. Of course, such a catalytic activity concerning chemical reactions with the dye, the electrolyte and additives, is a source for degradation in the DNSC. That Pt might be released under working conditions has been described in the literature. This pathway of instability depends, however, on the preparation method of the platinized counter-electrode [55].

So far, little attention has been paid to points 3 and 4 above. One contribution describes a poisoning of the Pt when stored in air, which was concluded from an increase of the charge transfer resistance [56]. If similar adsorption processes take place inside the cell, remains unclear. Nevertheless, they should be taken into account when failure analysis of, e.g., a production process is performed.

Beside Pt, a carbon counter electrode has been used occasionally [16, 17, 43, 57]. So far no indications are

published pointing towards stability problems, though similar mechanisms as described for Pt should apply.

3.5. Dye

3.5.1 Ru-complexes

Of all components in the DNSC, the dye has received most attention in the discussions related to stability. Already in 1979, the particular durability of Ru complexes as dye sensitizers in combination with TiO_2 was stressed [3]. Later, when Grätzel and O'Regan presented the nano-structured system in 1991, the stability of the trimeric ruthenium complex, which served as dye sensitizer in the DNSC, was discussed [4]: The authors presented that over a period of 2 months the photocurrent decreased by less than 10% when illuminated with visible light ($\lambda > 400\,nm$). The number of turnovers for the dye was estimated to 5×10^6. Similar results were achieved later for the monomeric dye cis-Ru(bpca)$_2$(SCN)$_2$. The authors claimed that the dye sustains more than 10^7 turnovers without significant degradation [5]. In particular, for the monomeric dye, the stability is surprising because it was shown earlier that the complex cis-Ru(bpy)$_2$(SCN)$_2$ (bpy = 2,2'-bipyridine) undergoes photo-induced replacement of the SCN^- ligand [58]. Generally, it was shown that mono-dentate ligands in Ru complexes are easily replaced, under irradiation, by solvent molecules due to population of anti-bonding orbitals [59]. It was postulated that the rapid injection into the conduction band of the TiO_2 suppresses the abstraction of the SCN^- ligands.

These results were challenged by Grünwald and Tributsch, who described degradation mechanisms for the trimeric as well as for the monomeric complex [7]. Based on in-situ IR experiments, it was proposed that the trimeric Ru complex is fragmented due to the photo-induced oxidation. Also, a ruthenium fragment of cis-Ru(bpca)$_2$(SCN)$_2$ leaves the surface and is therefore irreversibly lost for the DNSC. The authors explain this degradation by an incomplete reduction of the photo-oxidized dye by the I^-/I_3^- redox couple in combination with the instability of the oxidized form of the complexes. This investigation was questioned by Kohle and co-authors [8]. It was mentioned that the instability of the Ru sensitizers was due to a too low iodide concentration. According to the study by Kohle et al., in solution, under light irradiation and without the iodide as reducing agent, the thiocyanato is transformed into a cyano ligand, whereas on the TiO_2 surface with a sufficient iodide concentration, this process is completely suppressed. A somewhat different result was the outcome of a resonance Raman spectroscopy study [60]: It was shown that the SCN^- ligand can be detached from the cis-Ru(bpca)$_2$(SCN)$_2$ complex. It was also demonstrated that the additive 4-tert-
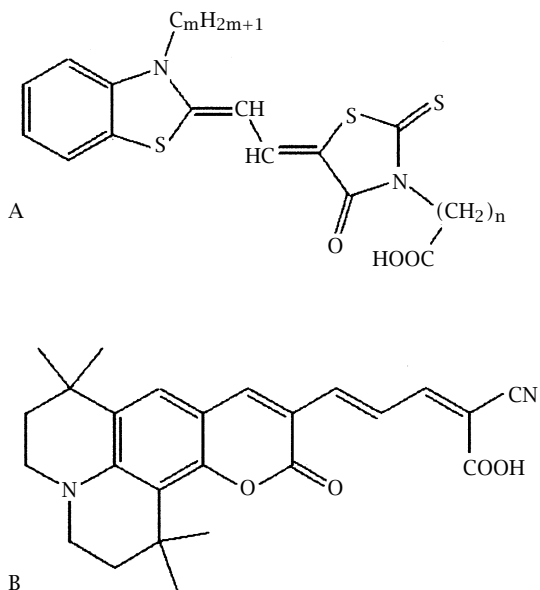

Figure 6. *Structures of merocyanine (A) and coumarin dyes (B).*

butylpyridine prevents to a large extent the ligand exchange. It has to be stressed that the light intensity of the applied laser in the Raman experiment was 10^6 times higher than full sunlight. Processes could therefore be triggered, which will not take place under outdoor working conditions.

Lately an alternative Ru complexes was presented, which incorporated hydrophobic substituents on one of the bpy ligands. The study showed that the desorption from the surface at elevated temperatures and triggered by water is prevented due to the amphiphilic properties of the Ru-dye sensitizer [12, 61].

3.5.2 Alternative dyes

An increasing number of dyes has appeared over the last few years trying to challenge the Ru complexes [47, 62–65]. Many of these dyes are so-called "organic dyes" since the molecules do not include a metal center. Already at a very early stage of the investigation of dye-sensitized semiconductor electrodes, the problem of instability of the dye was mentioned [66, 67]. It is also well known that most of the organic dyes rapidly undergo photo-oxidation when they are bound to the TiO_2 surface. This degradation is mainly triggered by the reactivity of the radical and the oxidized species produced due to light excitation and injection into the TiO_2 [34].

In order to stabilize the sensitizer one has to make sure that the electron injection and the recovery of the oxidized form by the redox couple are fast enough to suppress side reactions. Two groups of dyes have lately shown significant efficiencies: Modified coumarin dyes and merocyanine dyes (Figure 6) were tested for more

than 1000 hours at AM 1.5 with promising stabilities. One can conclude that the processes of injection and recovering are both very efficient, leading to the high stability as well as to high efficiencies.

3.6. Role of additives.

A number of additives, components, which do not participate in the fundamental photo-electrochemical processes as it is depicted in Figure 1, have been presented in the literature, which improve the efficiency and/or the stability. A group of compounds having a big effect on stability by many means, are nitrogen heterocycles like pyridine derivatives (e.g., 4-*tert*-butylpyridine) or imidazoles (e.g., 1-methylbenzimidazole): 4-tert-butylpyridine is able to improve the durability of the DNSC in the presence of water [9–11]. So far, the authors could not give an explanation for this fact. A hint was given by HPLC experiments, which showed a by-product appearing with time in the electrolyte when there is water and no 4-*tert*-butylpyridine present. Still, the degradation product has not been identified [11]. It can be speculated that the pyridine derivatives adsorb onto the TiO_2 surface slowing down the rate of the back-electron transfer [68]. As a result the production of aggressive radicals resulting from oxygen or water reduction is decreased. Although speculative, the results of these experiments are in total agreement with our own observation: Cells on plastic substrate, for which a high water content must be assumed, are relatively stable with the addition of 1-methylbenzimidazole added. 4-tert-butylpyridine on the other side gave not such a distinct effect since it evaporated from the cells [20]. Another stabilizing effect of additives might arise from the compensation of evolving Ti^{4+} ions according to the observed increase of surface states (see Section 3.2). Pyridine coordinates to Ti^{4+} and is therefore able to compensate the electron deficiency. Finally, the pyridine derivatives are assumed to stabilize *cis*-Ru(bpca)$_2$(SCN)$_2$ by preventing the loss of SCN^- [60, 69].

Another substance reported to be beneficial for the stability of the DNSC is MgI_2 and also CaI_2 [9]. Cells incorporating these salts showed remarkable stability towards UV-light radiation. An explanation for this fact could not been given yet.

4. CONCLUSIONS

4.1. Testing guidelines.

As mentioned in the introduction, a lifetime for DNSCs of 10 years and more is necessary to be able to compete with established commercial techniques. On the other side, a real-time testing of 10 years counteracts a rapid commercialization of the DNSC. Therefore, an accelerated testing is desirable and has been approached by a few groups [6, 8–11, 16]. Most remarkable is the investigation by Grätzel et al. showing cells with no degradation for a period of 1000 hours at 80 °C and light soaking [12].

Accelerated testing generally bears a challenge for the DNSC because of the delicate equilibrium of kinetic and thermodynamic parameters. The limitations and obstacles for accelerated testing can be exemplified by the approach to simulate long-term working conditions by the exposure to light intensities exceeding natural sunlight: For the DNSC, the I_{SC} saturates at high light intensities, depending on the kinetics and the diffusion within the cell. Illumination beyond the linear part of the current versus light function leads to an insufficient recovery of the dye resulting in long-lived instable oxidized dyes. It is also suspected that side reactions take place at high charge carrier concentration [16]. These processes are not expected to happen at normal sunlight and therefore many years of operation cannot be compared with a testing for a short period of time at artificially high light intensities. Additionally, in our own laboratories we have observed that cells, which are kept at intensities within the saturation part of the current-light function, recover to a large extent when they are kept in the dark (Figure 7).

Further experiments need to be performed to explain this behaviour. Nevertheless, it could indicate that cells exposed to day-night-cycles could be more stable than tests under continuous illumination indicate. This points out once more that results from light soaking experiments could underestimate the lifetime of DNSCs.

A particular problem of the DNSC is the large number of components in combination with the on-going search for alternatives improving the overall efficiency of the cells: Replacing components makes it necessary to freshly evaluate the stability, since the complex mechanisms at work allow only limited predictions about the influence of new components on the stability. The difficulties to accelerate tests in combination with the impractical real-time testing demands alternative techniques, which are able to make predictions about the lifetime. In our opinion, this can only be achieved by a fundamental understanding of degradation mechanisms in combination with a precise analysis of the cells under investigation. In other words, the aim must be to detect degradation before the performance (V_{OC}, I_{SC}, FF, η) of the cell decreases. The identification of parameters characteristic for destruction will follow from the understanding of degradation mechanisms and empirical investigations. A few examples and suggestions are given as follows:

During the lifetime of a cell a number of parameters should be monitored, which could indicate a failure. One of these parameters could be simply the weight of the cell in order to test the sealing quality. It might be combined with the application of vacuum in order to rapidly identify a leakage. A more elaborated approach to test the quality of a DNSC and to predict developments was published by Macht et al., who used space-resolved photocurrent imaging techniques adopted from the semiconductor industry [37]. With
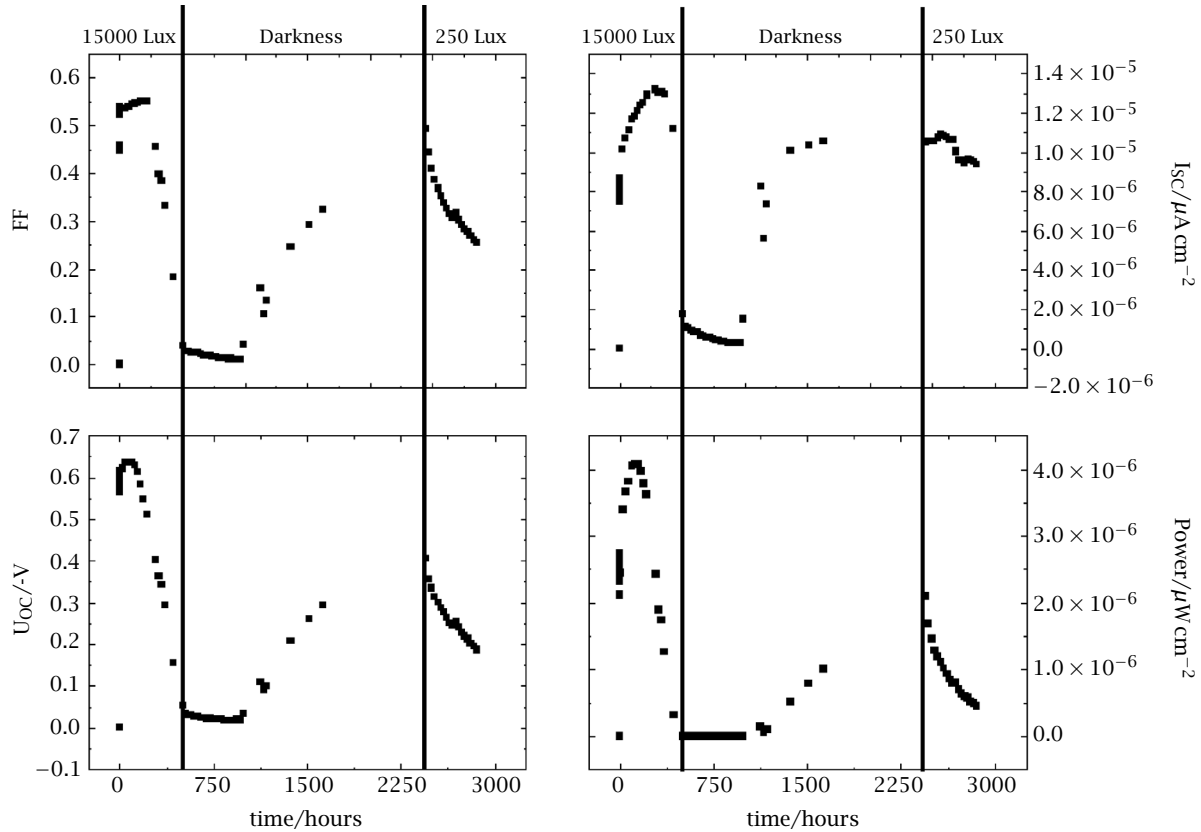
Figure 7. *Evolution of solar cell parameters with time (cis-*Ru(bpca)$_2$(SCN)$_2$*, 0.5 M NaI, 0.05 M* I$_2$*, 1-methylbenzimidazole in polyethylene glycol). The DNSC was stored at different light intensities as indicated. All measurements were performed at a light intensity of* 250 *Lux.*

this technique the authors were able to detect in an early phase of the cell's lifetime irregularities of the photocurrent within the cell area; e.g., leakage of solvent could be detected by significant patterns of the signal at the cell edges.

For predicting failure in an early stage of the use of a DNSC device, one has to determine intrinsic parameters like the kinetics of electron transfer processes or charge-transfer resistances.

A method already used for complementing stability experiments is impedance spectroscopy [41]. The authors determined series resistances in the cell as a function of time and a correspondence was found to the decrease of the I$_{SC}$. A further development of this method could enable a prediction of photocurrent losses in an early stage. Photo- induced absorption (PIA) can also be considered as a non-destructive method for probing the back-electron transfer rate. An early detection of the rate for this reaction seems to be an important step to predict the fate of DNSCs [70]. Generally, methods determining kinetic parameters of complete DNSC devices to include all types of interactions under normal solar light conditions are useful for monitoring DNSCs in order to anticipate failure. Another approach for which

we could not find any presentations in the literature includes the use of chemical sensors, which are able to interact with degradation products to produce an electrical or optical signal when degeneration takes place. Generally, the development of such methods is a great challenge and of great use in integrated chemical systems like the DNSC.

Finally, one could expose cells to different conditions like high light intensities and temperatures. After the exposure, the electrolyte could be extracted and analysed in order to detect degradation products, which could lead in the long-term perspective to cell failure although the cell parameters (V$_{OC}$, I$_{SC}$, FF, η) have not shown a decrease. In the same manner other components like the dye and the TiO$_2$ could be analysed. Of course, these tests are destructive and it is preferable to apply in-situ methods for which the on going testing of the cells does not need to be terminated.

4.2. Stabilizing DNSCs.
According to the analysis of the components, a number of suggestions for achieving stable DNSCs can be given. The interface between the nano-structured TiO$_2$ and the electrolyte seems to

be most crucial for the stability of the DNSC. One needs to prevent the adsorption of any kind of pollutants as described above, which could shift the Fermi level, trigger back-electron transfer reactions, etc.. In this respect, a blocking layer of insulating metal oxides seems to be a promising route not only to improve efficiency but also to ensure a constant power output [24, 25, 71]. Another positive effect of an insulating layer is the reduced back-electron transfer from the conduction band to species in the electrolyte. As pointed out, conduction band electrons in combination with oxygen can produce highly reactive H_2O_2. A layer separating the TiO_2 from the electrolyte most likely also reduces the reactivity of valence band holes. Therefore, UV light might have a less destructive impact.

Another key factor is the sealing of the cell since water and/or oxygen are highly destructive in particular at high light intensities. In combination with surface states and back-electron transfer reactions, oxygen could be transferred into a highly reactive radical, attacking all organic components in the cell [34]. It can be concluded that oxygen is a more severe problem for the stability of the cell than water, in particular in combination with high light intensities. In this context it can be suggested that radical scavengers could be applied like in food industry (anti-oxidants) in order to stabilize the cell. Generally, additives can beneficially be used to improve the stability in the way it was described for 4-*tert*-butylpyridine and MgI_2.

A UV-cut-off filter as many research groups are using seems to be essential in order to prevent band-gap excitation, resulting in TiO_2 mediated oxidation processes. These processes certainly lead to degradation of the organic components of the cell, including the dye and the solvent.

Of relevance is also the production method of the platinized counter-electrode: The numerous ways of destructive influences of Pt as described before (see Section 3.4) implies that the processing of the Pt must be very carefully performed in order to prevent release of Pt atoms and fragments [55].

4.3. Concluding remarks. The presentation of a dye-sensitized nano-structured photoelectrochemical solar cell with competitive light-to-energy conversion efficiencies has raised the question how stable these devices can be in practice. In the last decade, a significant number of contributions have been published, dealing with device testing and components analyses towards degradation. Despite controversial opinions and despite the complexity of the system, stabilities for a number of years have been proven. The most recent evaluations suggest that a lifetime of 10 years under outdoor conditions is within reach [12]. Nevertheless, it is also clear that the number of possible degradation mechanism is very high and that the system is only stable when the kinetic and thermodynamic parameters

are in a careful balance. These requirements are also responsible for the problems of using accelerated tests, as shown for the attempts to extrapolate data achieved at artificially high light intensities.

Standard procedures, new measurement techniques and improved fundamental understanding of the internal mechanisms need to be explored and applied by researchers and developers for a continuing successful development of DNSCs.

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REFERENCES

[1] A. J. Bard, Integrated Chemical Systems - A Chemical Approach to Nanotechnology, John Wiley & Sons, Inc., New York, 1994.

[2] K. S. C. Babu, O. N. Srivastava, and G. V. S. Rao, Current Science **66** (1994), 715.

[3] S. Anderson, E. C. Constable, M. P. Dareedwards, J. B. Goodenough, A. Hamnett, K. R. Seddon, and R. D. Wright, Nature **280** (1979), 571.

[4] B. O'Regan and M. Gratzel, Nature **353** (1991), 737.

[5] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-baker, E. Muller, P. Liska, N. Vlachopoulos, and M. Gratzel, Journal of the American Chemical Society **115** (1993), 6382.

[6] A. Kay and M. Gratzel, Solar Energy Materials and Solar Cells **44** (1996), 99.

[7] R. T. H. Grünwald, J. Phys. Chem. B **101** (1997), 2564.

[8] O. Kohle, M. Gratzel, A. F. Meyer, and T. B. Meyer, Advanced Materials **9** (1997), 904.

[9] A. Hinsch, J. M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer, and J. Ferber, Progress in Photovoltaics **9** (2001), 425.

[10] R. Kern, N. Van Der Burg, G. Chmiel, J. Ferber, G. Hasenhindl, A. Hinsch, R. Kinderman, J. Kroon, A. Meyer, T. Meyer, R. Niepmann, J. Van Roosmalen, C. Schill, P. Sommeling, M. Spath, and I. Uhlendorf, Opto-Electronics Review **8** (2000), 284.

[11] E. Rijnberg, J. M. K., J. Wienke, A. Hinsch, J. A. M. van Roosmalen, W. C. Sinke, B. J. R. Scholtens, J. G. de Vries, C. G. de Koster, A. L. L. Duchateau, I. C. H. Maes, H. J. W. Henderickx, Proceedings of the 2nd World Conference PVSEC - Vienna **47** (1998).

[12] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, and M. Gratzel, Nature Materials **2** (2003), 402.

[13] W. Kubo, K. Murakoshi, T. Kitamura, Y. Wada, K. Hanabusa, H. Shirai, and S. Yanagida, Chemistry Letters (1998), 1241.

[14] W. Kubo, Y. Makimoto, T. Kitamura, Y. Wada, and S. Yanagida, Chemistry Letters (2002), 948.

[15] W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada, and S. Yanagida, Chemical Communications (2002), 374.

[16] H. Pettersson and T. Gruszecki, Solar Energy Materials and Solar Cells **70** (2001), 203.

[17] H. Pettersson, T. Gruszecki, L. H. Johansson, and P. Johander, Solar Energy Materials and Solar Cells **77** (2003), 405.

[18] P. M. Sommeling, M. Spath, J. A. M. van Roosmalen, T. B. Meyer, A. F. Meyer, and O. Kohle, Dye Sensitized Nanocrystalline TiO_2 Solar Cells on Flexible Substrates, In 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion Vienna, 1998.

[19] H. Lindstrom, A. Holmberg, E. Magnusson, S. E. Lindquist, L. Malmqvist, and A. Hagfeldt, Nano Letters **1** (2001), 97.

[20] E. Figgemeier, G. Boschloo, V. Aranyos, E. Magnusson, A. Holmberg, H. Lindstrom, E. Pettersson, and A. Hagfeldt (unpublished results).

[21] A. Kraft, H. Hennig, A. Herbst, and K. H. Heckner, Journal of Electroanalytical Chemistry **365** (1994), 191.

[22] J. Moser, S. Punchihewa, P. P. Infelta, and M. Gratzel, Langmuir **7** (1991), 3012.

[23] R. Memming, Semiconductor Electrochemistry, Wiley-VCH, Weinheim, 2001.

[24] A. Kay and M. Gratzel, Chemistry of Materials **14** (2002), 2930.

[25] E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz, and J. R. Durrant, Journal of the American Chemical Society **125** (2003), 475.

[26] T. S. Kang, K. H. Chun, J. S. Hong, S. H. Moon, and K. J. Kim, Journal of the Electrochemical Society **147** (2000), 3049.

[27] J. Moser, S. Punchihewa, P. P. Infelta, and M. Gratzel, Langmuir **7** (1991), 3012.

[28] J. Bisquert, A. Zaban, and P. Salvador, Journal of Physical Chemistry B **106** (2002), 8774.

[29] G. Schlichthorl, S. Y. Huang, J. Sprague, and A. J. Frank, Journal of Physical Chemistry B **101** (1997), 8141.

[30] G. Boschloo and D. Fitzmaurice, J. Phys. Chem. B **103** (1999), 2228.

[31] M. R. Hoffmann, S. T. Martin, W. Y. Choi, and D. W. Bahnemann, Chemical Reviews **95** (1995), 69.

[32] S. T. Martin, H. Herrmann, W. Y. Choi, and M. R. Hoffmann, Journal of the Chemical Society-Faraday Transactions **90** (1994), 3315.

[33] S. T. Martin, H. Herrmann, and M. R. Hoffmann, Journal of the Chemical Society-Faraday Transactions **90** (1994), 3323.

[34] C. C. Chen, X. Z. Li, W. H. Ma, J. C. Zhao, H. Hidaka, and N. Serpone, Journal of Physical Chemistry B **106** (2002), 318.

[35] J. van de Lagemaat, K. D. Benkstein, and A. J. Frank, Journal of Physical Chemistry B **105** (2001), 12433.

[36] F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, P. Bogdanoff, and A. Zaban, Journal of the Electrochemical Society **150** (2003), E293.

[37] B. Macht, M. Turrion, A. Barkschat, P. Salvador, K. Ellmer, and H. Tributsch, Solar Energy Materials and Solar Cells **73** (2002), 163.

[38] D. J. Fitzmaurice, E. M., H. Frei, and J. Moser, Journal of Physical Chemistry **97** (1993), 3806.

[39] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhote, H. Pettersson, A. Azam, and M. Gratzel, Journal of the Electrochemical Society **143** (1996), 3099.

[40] S. Yanagida, S. Kambe, W. Kubo, K. Murakoshi, Y. Wada, and T. Kitamura, Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics **212** (1999), 31.

[41] C. Longo, J. Freitas, and M. A. De Paoli, Journal of Photochemistry and Photobiology a-Chemistry **159** (2003), 33.

[42] B. O'Regan, F. Lenzmann, R. Muis, and J. Wienke, Chemistry of Materials **14** (2002), 5023.

[43] G. K. R. Senadeera, P. V. V. Jayaweera, V. P. S. Perera, and K. Tennakone, Solar Energy Materials and Solar Cells **73** (2002), 103.

[44] D. Gebeyehu, C. J. Brabec, and N. S. Sariciftci, Thin Solid Films **403** (2002), 271.

[45] G. Kumara, A. Konno, G. K. R. Senadeera, P. V. V. Jayaweera, D. De Silva, and K. Tennakone, Solar Energy Materials and Solar Cells **69** (2001), 195.

[46] B. O'Regan, D. T. Schwartz, S. M. Zakeeruddin, and M. Gratzel, Advanced Materials **12** (2000), 1263.

[47] B. Oregan and D. T. Schwartz, Chemistry of Materials **7** (1995), 1349.

[48] M. Kaneko, K. Takayama, S. S. Pandey, W. Takashima, T. Endo, M. Rikukawa, and K. Kaneto, Synthetic Metals **121** (2001), 1537.

[49] S. Spiekermann, G. Smestad, J. Kowalik, L. M. Tolbert, and M. Gratzel, Synthetic Metals **121** (2001), 1603.

[50] D. Gebeyehu, C. J. Brabec, N. S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F. Kienberger, and H. Schindler, Synthetic Metals **125** (2001), 279.

[51] J. Disdier, J.-M. Herrmann, and P. Pichat, J. Chem. Soc. Faraday Trans. 1 **79** (1983), 651.

[52] P. Pichat, M.-N. Mozzanega, J. Disdier, and J.-M. Herrmann, Nouv. J. Chim. **11** (1982), 559.

[53] S. Sato and J. M. White, Chemical Physics Letters **72** (1980), 83.

[54] A. L. Linsebigler, G. Q. Lu, and J. T. Yates, Chemical Reviews **95** (1995), 735.

[55] E. Olsen, G. Hagen, and S. E. Lindquist, Solar Energy Materials and Solar Cells **63** (2000), 267.

[56] A. Hauch and A. Georg, Electrochimica Acta **46** (2001), 3457.

[57] A. Kay and M. Grätzel, Solar Energy Materials and Solar Cells **44** (1996), 99.

[58] P. E. Hoggard and G. B. Porter, Journal of the American Chemical Society **100** (1978), 1457.

[59] R. J. Forster, E. Figgemeier, A. C. Lees, J. Hjelm, and J. G. Vos, Langmuir **16** (2000), 7867.

[60] H. Greijer, J. Lindgren, and A. Hagfeldt, Journal of Physical Chemistry B **105** (2001), 6314.

[61] V. Aranyos, J. Hjelm, A. Hagfeldt, and H. Grennberg, Dalton Transactions (2003), 1280.

[62] K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, and H. Arakawa, Journal of Physical Chemistry B **106** (2002), 1363.

[63] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa, Solar Energy Materials and Solar Cells **77** (2003), 89.

[64] P. M. Jayaweera, S. S. Palayangoda, and K. Tennakone, Journal of Photochemistry and Photobiology a-Chemistry **140** (2001), 173.

[65] Q.-H. Yao, L. Shan, F.-Y. Li, D.-D. Yinb, and C.-H. Huang, New Journal of Chemistry **8** (2003), 1277

[66] H. Tributsch and M. Calvin, Photochem. Photobiol. **14** (1971), 95.

[67] H. Tributsch, Berichte Der Bunsen-Gesellschaft Fur Physikalische Chemie **73** (1969), 582.

[68] S. Y. Huang, G. Schlichthorl, A. J. Nozik, M. Gratzel, and A. J. Frank, Journal of Physical Chemistry B **101** (1997), 2576.

[69] H. Greijer, J. Lindgren, and A. Hagfeldt, Solar Energy, accepted for publication, 2003.

[70] G. Boschloo and A. Hagfeldt, Chemical Physics Letters **370** (2003), 381.

[71] B. A. Gregg, F. Pichot, S. Ferrere, and C. L. Fields, Journal of Physical Chemistry B **105** (2001), 1422.