

# Long-term Stability of Dye-Sensitised Solar Cells

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*Accelerated ageing tests on large numbers of nanocrystalline dye-sensitised solar cells (nc-DSC) show that, to first order, separation between the effects of the stresses of visible light soaking, UV illumination and thermal treatment on long-term stability is possible. The corresponding mechanisms are electrochemical, photochemical and purely chemical in nature. It was found that visible light soaking alone is not a dominant stress factor. A dramatic improvement in UV stability has been achieved by using MgI<sub>2</sub> as additive to the electrolyte. Thermal stress appears to be one of the most critical factors determining the long-term stability of nc-DSC and is strongly related to the chemical composition of electrolyte solvents and additives. Encouraging stability results have been obtained for cells based on pure nitrile-based solvents: (1) A minor decrease in performance of initially 5.5% solar efficient cells has been found after 2000 h at 60°C without light soaking; (2) After 900 h ageing at 85°C, a decrease of 30% in maximum power has been observed; (3) After 3400 h of combined thermal stress and continuous light soaking (45°C, 1 sun equivalent) good stability with 15% decrease in maximum power can be demonstrated. It should be noted that such good thermal stability has not been reported previously for dye-sensitised solar cells so far. Copyright © 2001 John Wiley & Sons, Ltd.*

## INTRODUCTION

Nanocrystalline dye-sensitised solar cells (nc-DSC) developed by Grätzel and co-workers<sup>1</sup> have achieved solar power efficiencies up to 10% on small areas.<sup>2,3</sup> Nc-DSC are photoelectrochemical solar cells. The photoelectrode of a nc-DSC consists of a thin film of porous nanocrystalline TiO<sub>2</sub> coated with a ruthenium metal–organic dye to absorb the light energy. Photoexcitation of the dye leads to injection of electrons into the conduction band of the oxide. The oxidised dye accepts electrons from iodide ions present in the electrolyte, and the resulting triiodide is reduced back to iodide ions at the platinum-coated counter-electrode. The electron injection from the dye into the TiO<sub>2</sub> is very efficient because of the fast kinetics (sub-picosecond scale) involved.<sup>4</sup> The resulting internal quantum efficiency is close to unity. Owing to the wide bandgap (3.2 eV) of the TiO<sub>2</sub> and the absence of holes, the electron lifetime in the nc-TiO<sub>2</sub> conduction

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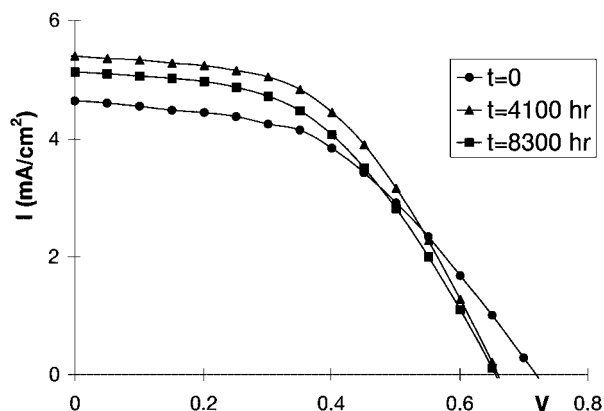


Figure 1. Current–voltage curves for low-efficiency (2%) nc-DSC single cell irradiated under continuous 2.5 sun equivalent light intensity at 20°C cell temperature. Cell composition: dye: N3, TiO<sub>2</sub>: P25 (Degussa); electrolyte: 0.4 M HMII (hexylmethylimidazolium iodide, 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.3 M TBP (4-*tert*-butylpyridine) in methoxypropionitrile solvent. I–V measurements by class A solar simulator (1000 W/m<sup>2</sup>) with no spectral mismatch correction

band is 10–50 ms, high enough to guarantee sufficient charge transport through the typically 10- $\mu$ m-thin TiO<sub>2</sub> film.<sup>5</sup> Both in terms of working principle and cell construction, nc-DSC are attractive because of their simplicity.

For successful use of nc-DSC for outdoor applications several factors are of importance, e.g., technical performance and manufacturability, costs, design, market demand and last but not least long-term stability. The overall stability of this cell is controlled by two factors, namely physical and chemical stability. Physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technological problem, for which solutions can be found by using suitable sealing materials and techniques.<sup>6–8</sup> The intrinsic chemical stability is related to irreversible (photo-) electrochemical and thermal degradation of the dye or electrolyte components, which might occur during operation of the cell.

#### *Preliminary stability studies*

In 1997, preliminary stability studies<sup>9,10</sup> were done on low-efficiency ( $\sim$ 2%) single cells. A result from these long-term light soaking experiments is shown in Figure 1. The cell temperature under strong visible illumination was 20°C in order to avoid thermal stress. The photon flux absorbed by the cells continuously during irradiation was equivalent to the effect under 2.5 sun illumination, excluding the ultraviolet region. There was a small decrease (50 mV) in open-circuit voltage after exposure for 8300 h, which was compensated by the increase in short-circuit current. These results motivated further investigations.

#### *Present approach*

The present work focuses on the intrinsic chemical stability of nc-DSC. Appropriate accelerated ageing test procedures for nc-DSC have to be developed so that useful extrapolations to real outdoor conditions can be made. Several stress factors can be distinguished and are applied to nc-DSC; visible light, UV light and temperature. We describe encouraging results gained from these stability tests thus far, and discuss the degradation mechanisms involved, together with present possible steps for further improvements.

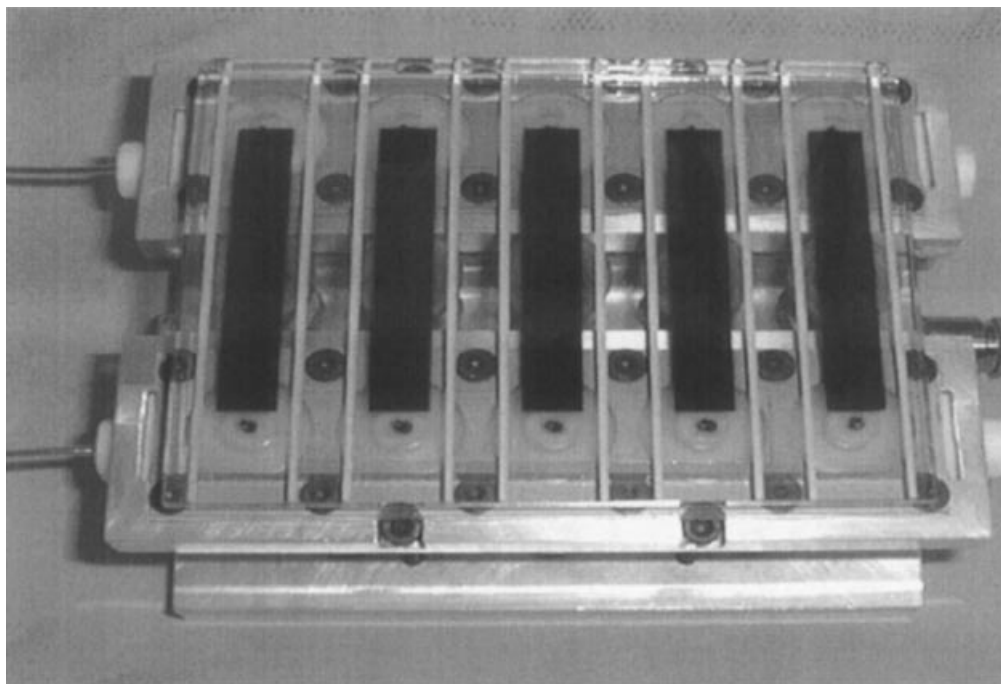


Figure 2. Fabrication of a masterplate (75 × 100 mm) containing five individual dye-sensitised test cells (active area 4 cm<sup>2</sup> each). The colouration step (flushing of dye solution after primary sealing through holes in a filling unit) is shown

## EXPERIMENTAL

### *Measurement object: masterplates*

The nc-DSCs for the stability tests are fabricated in all cases on so-called masterplates. These plates consist of five individual cells of 5 × 0.8 cm<sup>2</sup> on a common SnO<sub>2</sub>:F-glass substrate (LOF-TEC8, 3 mm, 8 Ω/square). TiO<sub>2</sub> layers are deposited by screen printing. The synthesis of the nc-TiO<sub>2</sub> particles and the formulation of a screen print paste are similar to those described earlier.<sup>11</sup> A screen-printed silver strip on each side of each cell ensures proper current collection within the masterplate. Also, SnO<sub>2</sub>:F-glass substrates coated by screen printing with a thin pyrolytic platinum layer are used as the counter-electrodes. Both electrodes are fired at 450–500°C for 30 min. Surlyn 1702 (DuPont) hotmelt foil has been used as the primary sealing material for cells aged below 60°C. The distance between the electrodes is approximately 25 μm in this case. A representative picture of a masterplate during fabrication is shown in Figure 2. In total, more than 100 masterplates have been manufactured in this manner. The sensitising dye used for the masterplates was *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylate)Ru(II) (N3) or its two-fold deprotonated form (N719). The dye is applied in most cases by refluxing a dilute solution of 1 mM dye in 50:50 acetonitrile/*tert*-butanol through the cells at 40°C for 30–60 mins.

Cells which undergo stability tests above 60°C cannot be sealed with Surlyn 1702, hotmelts with higher melting points or hermetic sealing materials are required. In particular, a different sealing technique has been developed which makes use of a low-melting-temperature glass frit. The composition of the glass frit has been carefully adjusted to match the thermal expansion coefficient of the glass plates. The actual sealing (fusing) of the masterplates takes place at 650°C for several minutes. No mechanical pressure is applied during the fusion step. Also, a modified coloration solution is applied in this case, consisting of a more concentrated solution (5 mM) of N719 in a 3:1 acetonitrile *tert*-butylpyridine mixture. After application of the electrolyte, the

Table I. Reproducibility efficiency of two masterplates

Masterplate cell number	$I_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	Efficiency at 1000 W/m <sup>2</sup> (%)
4408-1	10.54	0.679	65.9	4.7
4408-2	10.94	0.672	66.0	4.8
4408-3	12.12	0.670	66.0	5.4
4408-4	11.20	0.667	66.7	5.0
4408-5	12.12	0.665	65.5	5.4
4401-1	12.25	0.705	56.0	4.8
4401-2	11.85	0.703	58.1	4.8
4401-3	11.69	0.700	57.6	4.7
4401-4	12.20	0.697	56.9	4.8
4401-5	12.39	0.690	62.0	5.3

filling holes are carefully sealed with the help of a hotmelt foil made from Bynel (DuPont) and a thin glass cover.

The masterplate concept was chosen in order to be able to obtain reliable and reproducible results, which is necessary in stability tests. Table I shows efficiency data of two different masterplates sealed with Surlyn. The results indicate that, for all measured photovoltaic parameters, reproducibility for five cells on one masterplate can be achieved within  $\pm 7.5\%$ . In the case of glass frit-sealed masterplates similar performance is achieved. It should be mentioned that the cell design used in the present work has not been optimised for high efficiency. In particular the distance (12 mm) between the current-collecting silver fingers, and therefore the series resistance in the TCO layer, is too large, resulting in rather low fill factors.

#### Characterisation and ageing

Continuous strong light soaking and on-line characterisation of photovoltaic parameters has been done at identical sites<sup>12,13</sup> (Figure 3) at the laboratories of the individual authors. For a long-term stable light source sulphur plasma lamps are used. The sulphur lamp spectrum is continuous from 400 to 800 nm, with its

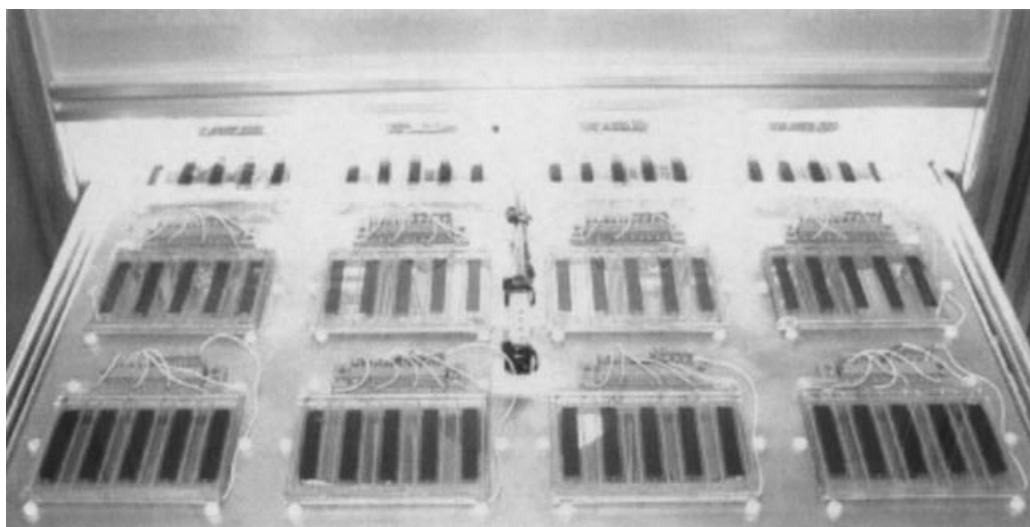


Figure 3. Continuous illumination and characterisation sites for simultaneous light soaking experiments. At each site, 16 masterplates containing in total 80 test cells are operated under 1 Sun equivalent sulphur lamp spectra. Masterplates in opened drawer are shown. Six such sites have been installed at the project partners

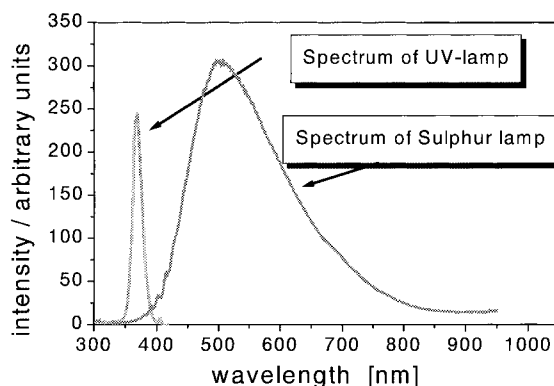


Figure 4. Spectra of the UV lamps and the sulphur vapour lamp used in the UV and visible light soaking tests

maximum at 500 nm, approximating quite well the solar spectrum in the spectral sensitivity range of the nc-DSC. The lamp spectrum contains practically no UV light below 400 nm. Silicon reference cells control the lamp intensity. Every week, the cells are automatically characterised at the illumination sites. Data is electronically transferred to a central database at FMF Freiburg. In order to handle the large amounts of data, MS SQL-Server is used as the database management system. Ageing under UV light is done with densely packed UV-emitting fluorescent tubes (UV-TLD18W/08, Philips). The UV lamp spectrum is continuous, from 345 to 400 nm and matches the photoactivity spectrum of  $\text{TiO}_2$  in the cell. The UV intensity is  $5 \text{ mW/cm}^2$  in the sample area. Figure 4 shows the spectra of the UV lamp and the sulphur lamp. The cell temperature under the UV lamp is kept constant at  $38^\circ\text{C}$ . Electrical impedance spectroscopy (EIS) is performed with an IM6 potentiostat (Zahner Electric). Degradation products in the electrolyte are detected by gas chromatography–mass spectroscopy (GC–MS).

## RESULTS

### *Light soaking at elevated temperatures*

More than 50 masterplates have been exposed to sulphur lamp irradiation in stability tests. The light intensity was adjusted to approximately 1 sun, at  $\approx 45^\circ\text{C}$ . Results obtained from these tests show some striking differences in stability when different electrolyte solvents are used. For instance, cells containing methoxyacetonitrile show poor stability behaviour under these conditions, while propionitrile seems to be a good choice of solvent for further research. In the latter case, a very small decrease of  $I_{\text{sc}}$  and a gradual decrease of  $V_{\text{oc}}$  over time is observed. A typical example for cells containing propionitrile-based electrolytes is shown in Figure 5, where after 3400 h of ageing, a decrease in maximum power of less than 15% has been deduced.

### *Testing under constant UV illumination*

Exposure to UV light has been found to be deleterious for some nc-DSC. Electrolyte additives can cause large differences in UV stability. The effects of addition of  $\text{MgI}_2$  and other additives, such as  $\text{CaI}_2$  and 2-phenylimidazole, to various electrolyte compositions have been studied, and some of these results are displayed in Figure 6. The electrolyte compositions are given in Table II. It can be seen that both  $\text{MgI}_2$  and  $\text{CaI}_2$  show strong UV-stabilising effects.

### *Analysis of thermal degradation*

In order to examine the influence of the temperature on the long-term stability of nc-DSC, masterplates are aged in hot-air convection ovens at different temperatures without light soaking. For cells containing

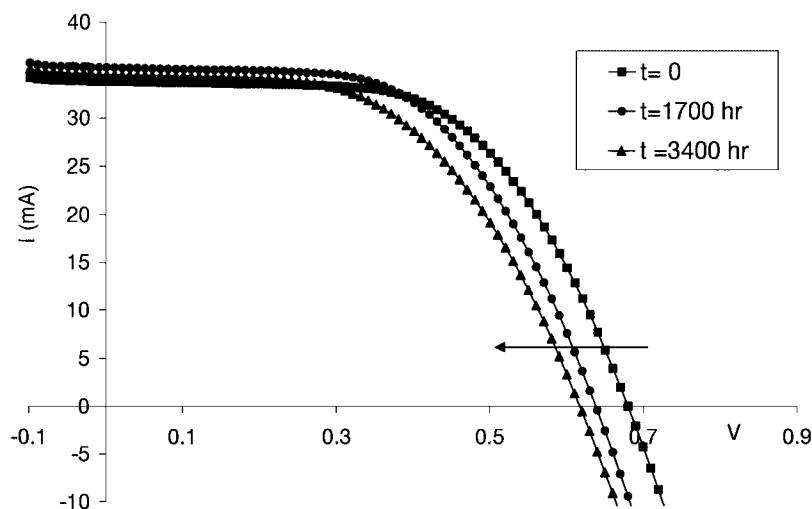


Figure 5. I–V results from 1 sun equivalent continuous light soaking at 45°C cell temperature. Electrolyte composition: 0.6 M HMII, 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.5 M TBP in propionitrile (chemicals used as received)

methoxyacetonitrile as the electrolyte solvent, strong degradation of performance was observed above 45°C. This was not the case for propionitrile as solvent (see below). In order to examine the possible origin of thermal degradation, the chemical composition of the aged electrolyte was analysed by GC–MS. The results are compiled in Figure 7. From the analyses it was found that methoxyacetamide (via hydrolysis of methoxyacetonitrile) was formed after thermal ageing. As can be seen in Figure 7, the amount of methoxyacetamide is strongly dependent on the storage temperature. Furthermore, methoxyacetamide was not detected in the electrolyte reference, but formed only in the solar cell, even to some extent after storage at 7°C.

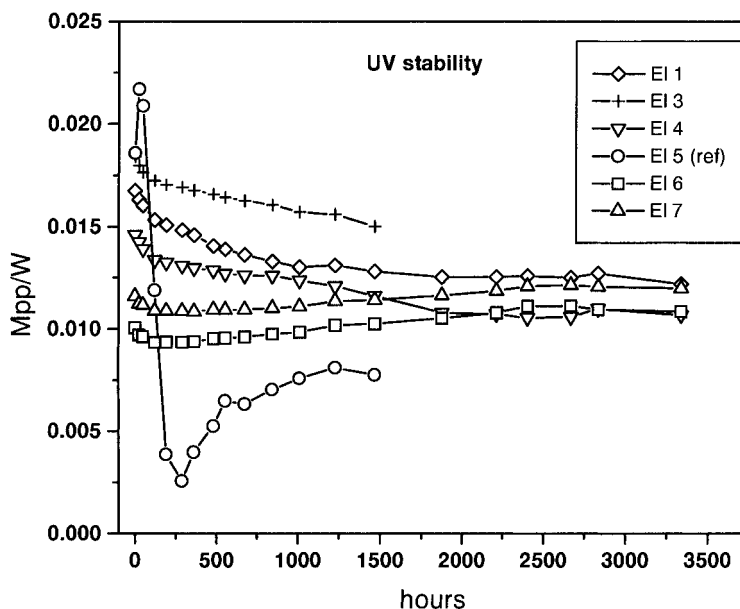


Figure 6. Stability data (maximum power measured under 1 sun) of cells on masterplates aged with a UV tester (cell temperature 38°C). Electrolyte 5 is the (unstable) reference without additive

Table II. Electrolyte compositions, notation as in Figure 5. Solvent in all cases acetonitrile.  $\text{MgI}_2$  and  $\text{CaI}_2$  dissolved at  $60^\circ\text{C}$  in a HMII/acetonitrile mixture prior to further dilution

Electrolyte	Compositions
El 1	0.5 M $\text{MgI}_2$ , 0.3 M HMII, 0.6 M TBP, 30 mM $\text{I}_2$
El 3	0.2 M $\text{CaI}_2(\text{aq})$ , 0.4 M HMII, 40 mM $\text{I}_2$ , 1.3 M TBP
El 4	0.6 M $\text{CaI}_2(\text{aq})$ , 0.3 M HMII, 40 mM $\text{I}_2$ , 1.3 M TBP
El 5	0.5 M HMII, 40 mM $\text{I}_2$ , 0.7 M TBP
El 6	0.2 M $\text{CaI}_2(\text{aq})$ , 50 mM $\text{I}_2$ , 0.42 M 2-phenylimidazole
El 7	0.2 M $\text{CaI}_2(\text{aq})$ , 0.5 M HMII, 50 mM $\text{I}_2$ , 0.42 M 2-phenylimidazole

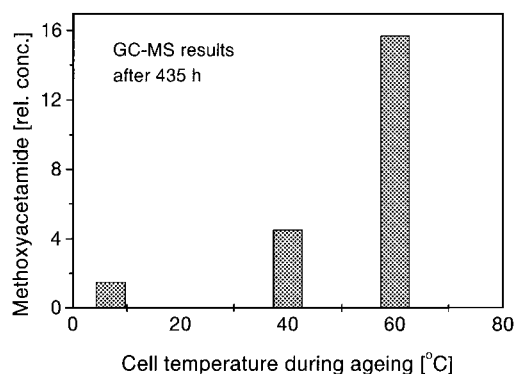


Figure 7. Relative amount of methoxyacetamide impurity in electrolyte as analysed with GC-MS after thermal stress test at 7, 40 and  $60^\circ\text{C}$  for 435 h. No impurity detected in reference electrolyte

In order to find physical explanations for the degradation behaviour, more characterisation methods are needed. Electrical impedance spectroscopy (EIS) has been shown to be a useful technique for the extraction of parameters determining the behaviour of nc-DSC. Observed changes in the EIS of nc-DSC after ageing can lead to a better understanding of the degradation phenomena of the cells. Figure 8 shows EIS spectra of a thermally unstable cell containing methoxyacetonitrile. Ageing has been carried out at  $60^\circ\text{C}$  for up to 435 h in the dark. The phase of the EIS under open-circuit conditions and full sun illumination is shown. It can be seen that the position of the main peak is shifted towards higher frequencies, indicating a decrease in lifetime of photogenerated electrons in the  $\text{TiO}_2$  conduction band.<sup>11</sup> As presented in Table III, a nonlinear correlation is observed between  $I_{\text{sc}}$  and the decrease in electron lifetime in the  $\text{TiO}_2$  photoelectrode during ageing at  $60^\circ\text{C}$ .

#### Best results from thermal ageing

Great effort has been made to stabilise the cells at temperatures of  $60^\circ\text{C}$  and above. The best results from thermal stress tests at  $60^\circ\text{C}$  achieved thus far are shown in Figures 9 and 10 for cells containing purified propionitrile as the electrolyte solvent. Almost no decrease in cell efficiency after 2000 h at  $60^\circ\text{C}$  is observed which is a very encouraging result. Since IEC norms<sup>14</sup> for crystalline solar cells require stability tests at  $85^\circ\text{C}$ , this condition was also applied to the dye-sensitised cells. To do this the sealing material of the standard configuration had to be changed. As described in the experimental section, a glass frit technique has been used in this case. The results are also displayed in Figures 9 and 10. After 875 h of thermal aging at  $85^\circ\text{C}$  a decrease of only 30% in cell efficiency has been observed. It should be noted that such high thermal stability has not been reported for dye-sensitised solar cells up to now.

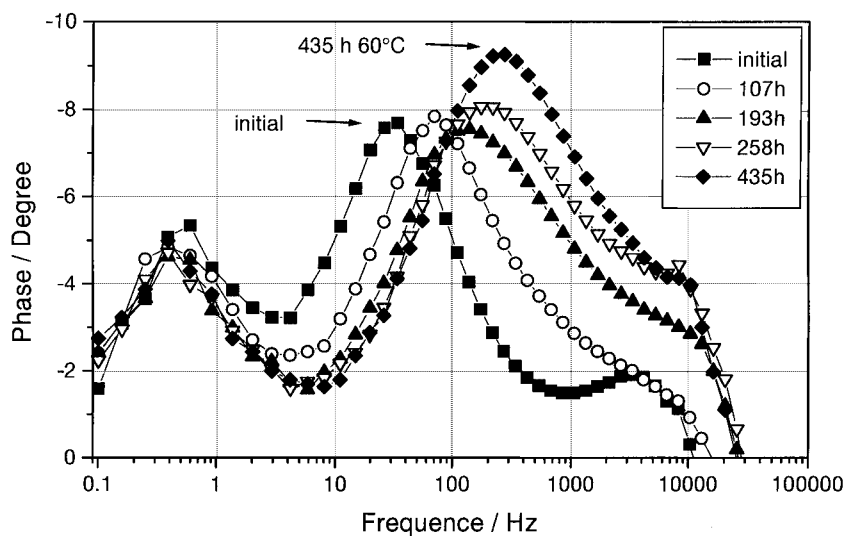


Figure 8. Results from electrical impedance spectroscopy EIS (phase shift, 1 sun illumination, open-circuit) on cells containing methoxyacetonitrile which have been aged at 60°C for up to 435 h without light soaking

Table III. Correlation between short-circuit current and electron lifetime in the TiO<sub>2</sub> photoelectrode, calculated from the main peak of the EIS measurement in Figure 8 for cells aged in the dark

Time (h)	Cell 450 aged at 7°C		Cell 465 aged at 40°C		Cell 470 aged at 60°C	
	$I_{sc}$ (mA/cm <sup>2</sup> )	$\tau_{el}$ (ms)	$I_{sc}$ (mA/cm <sup>2</sup> )	$\tau_{el}$ (ms)	$I_{sc}$ (mA/cm <sup>2</sup> )	$\tau_{el}$ (ms)
000	10.7	6.1	12.2	6.1	11.0	6.1
017			11.7	6.1	10.2	3.7
107	10.2	6.1	11.2	6.1	08.0	2.3
150	11.0	6.1	11.5	6.1	07.0	1.8
193	10.5	6.1	10.2	4.8	05.5	0.8
302	11.0	6.1	10.2	4.8	05.2	0.8
435	11.0	6.1	09.7	4.8	05.0	0.59

### Thermal ageing of cells at 85°C containing various electrolytes

Various cells containing different electrolytes have been tested at 85°C for 875 h in order to study the influence of electrolyte additives. Acetonitrile and propionitrile have been used as solvents. Some results and the electrolyte compositions are shown in Figure 11. Owing to the rather large statistical deviations in current after the test, it is difficult to see any effect of the electrolyte additives. A general trend is that, independent of the initial open-circuit voltage, after thermal ageing at 85°C the voltage drops to around 0.55 V. There is some indication that electrolyte B, containing MgI<sub>2</sub> and TBP, is the best choice so far.

## DISCUSSION

### Photo-electrochemical stability

Intense visible light soaking (2.5 sun sulphur lamp) alone is not a dominant stress factor for dye-sensitised solar cells. Remarkably, as predicted in the early days and doubted by many, the system is very regenerative in terms of photo-electrochemical stability, i.e. in number of redox cycles. As an explanation, the following mechanism

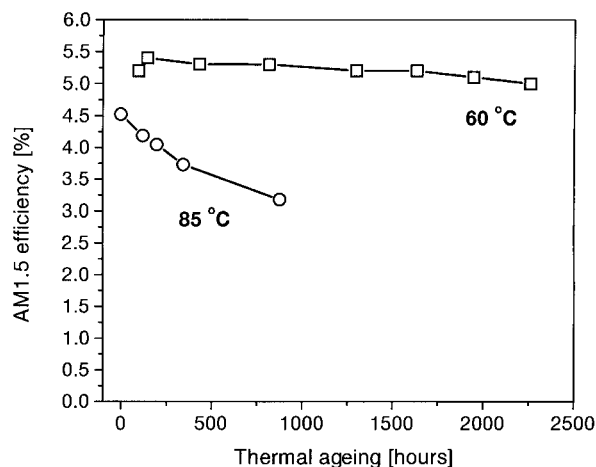


Figure 9. Best stability results (efficiency) achieved so far with thermal ageing at 60 and 85°C without light soaking. The electrolyte in the 60°C test is based on dimethylpropyl imidazolium iodide (DMPII), LiI, I<sub>2</sub>, TBP and propionitrile. In the 85°C test, the electrolyte also contained MgI<sub>2</sub> in the following composition: 1.5 M hexylmethylimidazolium iodide (HMII), 0.12 M MgI<sub>2</sub>, 0.02 M I<sub>2</sub>, 0.6 M TBP in propionitrile (PN) solvent. The PN solvent was purified before use

can be proposed: the photo-excited state of the dye is very rapidly (femtosecond range) quenched by electron transfer to the titanium dioxide. The oxidised dye molecules (ruthenium (III) centre) are then regenerated (reduced) by iodide from the redox couple in the electrolyte quickly enough to prevent non-regenerative side reactions.

There are also hypotheses that predict degradation under visible light.<sup>15</sup> One is that there will always be a small fraction of dye molecules that are not attached sufficiently strongly to the titanium dioxide surface to allow fast electron transfer of the excitation energy. These are molecules which are dissolved in the electrolyte solvent or molecules in higher molecular aggregates (double layers, etc.). It is therefore expected that dye molecules dissolved in the electrolyte are less photostable. Another factor often mentioned could be the exchange of SCN<sup>-</sup> ligands from the dye with the iodide ions or water residues during the lifetime of the excited state. Why such mechanisms have seemingly no great effect on the stability of dye-sensitised solar cells under visible light stress is not yet fully understood.

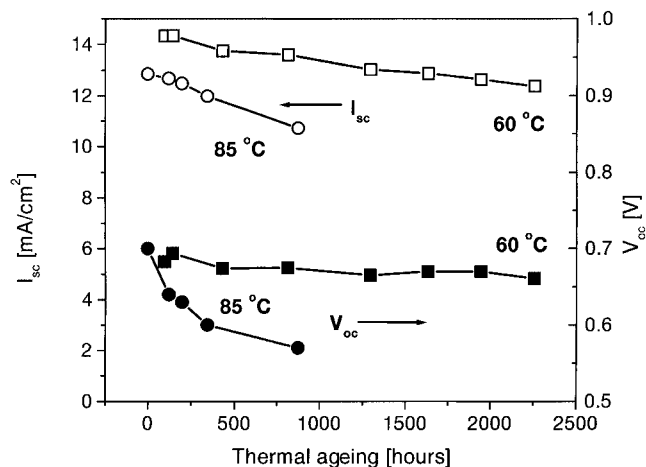


Figure 10. As for Figure 9, showing short-circuit current  $I_{sc}$  and the open-circuit voltage  $V_{oc}$

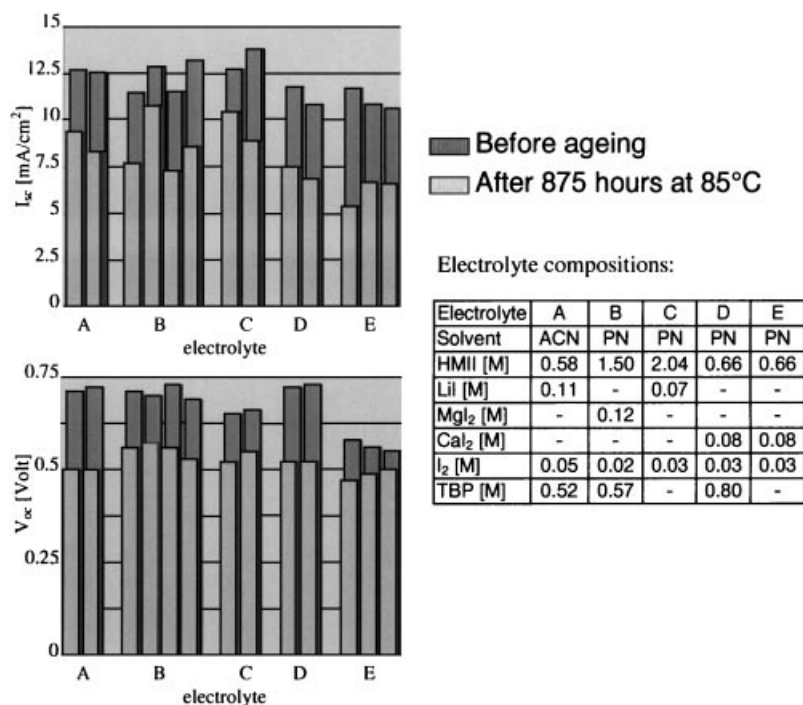


Figure 11. Results from a thermal ageing test performed on various cells on master plates containing different electrolytes. Short-circuit current and open-circuit voltage values before and after ageing at 85°C for 875 h are shown. Only cells that passed the visual inspection test (no major leakage of electrolyte) after ageing are shown. ACN acetonitrile; PN propionitrile; HMII hexylmethylimidazolium iodide; TBP *tert*-butylpyridine

#### Direct bandgap excitation under UV

UV light often has a negative effect on the stability of the electrolyte. One observation made by optical spectroscopy is that iodine, initially present in the electrolyte at 50 mM, is irreversibly consumed (bleached) under UV illumination. As iodine is necessary in the redox couple  $I^-/I_3^-$ , the electrolyte in this case becomes electrochemically blocking at the counter-electrode side. The explanation for the bleaching of the triiodide may be side reactions of photogenerated oxidative holes at the titanium dioxide surface. The corresponding electrons can then lead to a non-regenerative reduction (recombination) of the iodine to iodide at the counter-electrode, or more slowly at the photoelectrode. It should be noted that this is a likely, but still not proven hypothesis.

#### UV stabilisation of electrolyte with MgI<sub>2</sub>

Besides the option of applying UV filters (foils) as protection, our results demonstrate that certain electrolyte additives can dramatically increase the UV stability. The most effective additive found so far is MgI<sub>2</sub>. As is indicated from the lower photovoltage, Mg<sup>2+</sup> makes the TiO<sub>2</sub> surface more positive. Fortunately this effect can be compensated by enhancing the amount of *tert*-butylpyridine in the electrolyte without loss in photocurrent. It should also be noted that MgI<sub>2</sub> seems not to block the hole reactions at the titanium dioxide surface. MgI<sub>2</sub>-containing electrolytes in cells with photoelectrodes but without dye coating show a good photocurrent under UV illumination caused solely by direct bandgap excitation of the TiO<sub>2</sub>. There are several possible explanations for the enhanced stability: a faster reduction of the holes by iodide; the lower photopotential; or the formation of a MgO surface layer, preventing side reactions. CaI<sub>2</sub> seemingly also has a UV-stabilising

effect and requires less *tert*-butylpyridine as a weak base additive to compensate for the voltage drop compared with  $\text{MgI}_2$ .

#### *UV stability of the dye*

As can be concluded from the quite stable photocurrent under UV illumination for cells containing  $\text{MgI}_2$ , the dye itself seems not to be attacked by the UV. This is quite striking, because free R-COOH groups, similar to the functional groups of the dye are known to be rapidly photo-oxidised on the titanium dioxide surface. Even in the presence of the iodide ion, which quenches the oxidative hole in the titanium dioxide valence band, some side reactions with oxygen residues, leading to destruction of the surface groups, could be considered. Therefore there might also be stabilising mechanisms under UV illumination, as yet unknown. One possible mechanism to be considered for capturing the photo-oxidative electron vacancy (hole) at the  $\text{TiO}_2$  surface is the reversible oxidation of the Ru(II) centre of the dye itself.

#### *Electrolyte solvent*

Another unwanted side reaction under UV illumination is the photo-oxidation of the electrolyte solvents. This has forced us up to now to use UV-stable nitriles as electrolyte solvents. More electrolyte solvents and also gelled electrolytes have to be scanned in further experiments in combination with effective UV-stabilising additives such as  $\text{MgI}_2$ .

#### *Thermal activation energies*

The thermal stability is the most critical item. At least a single-exponential response of degradation rate to thermal stress can be expected. It is therefore crucial to define the relevant upper temperature in accelerated ageing for a correct extrapolation to long-term operation. As a guideline for the required thermal stress,  $80^\circ\text{C}$  for 1000 h should at least be targeted for mid-European locations. Up to now stability for 2000 h at  $60^\circ\text{C}$  and a 30% decrease in performance after 900 h at  $85^\circ\text{C}$  have been demonstrated. These results are very promising, but still not enough to give much information about thermal activation energies.

#### *Catalytic reactions*

It should not be forgotten that two catalysts ( $\text{TiO}_2$  and Pt) are present in the cell which could catalyse interactions, especially with the electrolyte solvent. It can be expected that, in the presence of the iodide/iodine redox couple, catalytic reactions are quenched, but to what extent is not known. Especially in the case of  $\text{TiO}_2$  a correlation between the amount of catalyst, i.e., the layer thickness, and the thermal stability is to be expected.

#### *Chemical nature of electrolyte solvent*

Another point is the chemical nature of the electrolyte solvent and its possible decomposition products and reaction routes when the electrolyte components are under thermal stress. Experiments have shown so far that pure nitrile-based solvents (acetonitrile, propionitrile) are the most stable. Solvents containing chemically bonded oxygen test as much less stable. It was described above that, after thermal aging of cells containing methoxyacetonitrile, methoxyacetamide was found as a degradation product. Residues of water in the solvent and on the  $\text{TiO}_2$  surface have probably caused this hydrolysis reaction. Nevertheless, solvents containing N-C=O bonds should be tested (again). Very contradictory results have been seen so far with  $\gamma$ -butyrolactone. A crucial issue to address in further experiments is therefore the purity of the solvent and inert handling during cell manufacture.

#### *Permeability of sealing material*

Under thermal stress above  $60^\circ\text{C}$ , the permeability of the standard sealing material (Surlyn) towards solvent, oxygen and humidity can become important, and can interfere with the 'internal' chemical stability. In this case

polymeric materials with a higher melting point, e.g., Bynel, or hermetic sealing materials such as glass frits have to be used.

#### *Short-circuit current after thermal stress*

Hypotheses for the decrease of the short-circuit current under thermal stress are:

- The reduction of the electron diffusion length in the titanium dioxide due to surface modifications (traps), weakening of the interparticle connections, or even changes in the TiO<sub>2</sub> crystal structure. In these cases, the injected electron remains trapped inside the titanium dioxide (or at the surface) which enhances the probability of recombination with triiodide in the electrolyte. As this recombination process takes place at the photoelectrode side and not at the counter-electrode, it results in a loss of external photocurrent. To first order, the external photovoltage is not affected. The EIS observations strengthen this hypothesis.
- Increased surface recombination due to surface-active decomposition products that contain iodine, in particular in the form of iodated organic species such as iodoacetic acid. In this case the dark current will also be enhanced, causing a drop in open photovoltage.
- Reduction of the electron injection efficiency of the dye due to dye degradation or changes in the dye absorption spectra (replacement of ligands).
- Side products in the aged electrolyte which quench (reduce) the oxidised dye state and are electrochemically concurrent with the iodide/I<sub>2</sub> reaction. These products are most likely longer-living radicals which also recombine (regenerate) with the iodide, but with time scales of seconds which are longer than those (10 ms) required for efficient charge transport under full-sun illumination.
- Decomposition products in the electrolyte co-adsorbing to the TiO<sub>2</sub> surface and causing partial desorption of the dye.
- Diffusion of platinum from the counter-electrode to the TiO<sub>2</sub> and/or TCO surface. As a result, an enhanced internal recombination current is to be expected.

#### *Open-circuit voltage after thermal stress*

Hypotheses for the decrease in open-circuit voltage under thermal stress are:

- Release of protons (acid formation) from the electrolyte solvent. In this case, a 'pH buffer' such as 4-*tert*-butylpyridine might be advantageous.
- Diffusion of platinum to the TCO (SnO<sub>2</sub>:F) surface resulting in a higher dark current and therefore lower open-circuit voltage.
- Formation of other side products on the TCO interface, lowering the over potential for electron transfer to triiodide. In both cases a thin underlayer of TiO<sub>2</sub> on the TCO might be advantageous.
- More generally it may well be that thermally induced changes at the TCO–electrolyte interface have a stronger influence on the open-circuit voltage than at the TiO<sub>2</sub> electrode layer.

## **CONCLUSIONS**

Accelerated ageing tests on large numbers of dye-sensitised solar cells show that, to first order, a separation between the effects of the stresses of visible light soaking, UV illumination and thermal treatment on the long-term stability is possible. The corresponding mechanisms are electrochemical, photochemical and purely chemical in nature.

Intense visible light soaking with 2.5 sun equivalent intensity is not a dominant stress factor. Cell stability up to 8300 h has been demonstrated under these conditions. Electrochemically, this result corresponds to a number of redox cycles equivalent to operation at least 10 years outdoor.

Our results on UV stabilisation have been very successful. A dramatic improvement in stability under strong UV illumination has been reached by using  $\text{MgI}_2$  as additive to the electrolyte; 3300 h, corresponding to at least 3 year outdoor operation with no additional UV filter! In combination with a simple UV-filtering top layer, dye-sensitised solar cells can therefore be UV stabilised for significant (10 year) long-term outdoor operation.

The long-term extrapolation of the thermal stability achieved so far is still of critical importance. Further experiments in the range 80–100°C still need to be made to learn more about thermal activation energies. Also, the upper module outdoor temperatures of nc-DSCs, depending on location and module mounting (roof, stand-alone, facade) have to be determined. Nevertheless, the results—a minor decrease for 5.5% solar efficient cells after 2000 h at 60°C and a 30% decrease in maximum power of 4.5% efficient cells after 900 h at 85°C—are very promising. For cells under combined thermal stress and light soaking (3400 h, 45°C) good stability with a 15% decrease in maximum power has so far been demonstrated. Under certain outdoor conditions, a preliminary extrapolation to 5 years stability can be drawn from these results. The effect of applying periodic stresses has not yet been studied. Physical failures, but also recovery phenomena are to be expected.

In general, the authors have the impression that long-term stability of dye-sensitised solar cells is not an intrinsic problem of the technology, but can be improved further by better understanding of the degradation mechanisms and chemical balancing of the electrolyte components.

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