

LONG-TERM STABILITY OF DYE SENSITIZED SOLAR CELLS FOR LARGE AREA POWER APPLICATIONS (LOTS-DSC)

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ABSTRACT: Accelerated ageing tests on large numbers of dye sensitised solar cells show, that to first order a separation between the effects of the stresses visible light soaking, UV-illumination and thermal treatment on long-term stability can be made. The corresponding mechanisms are of electrochemical, photochemical and pure chemical nature respectively. It was found that visible light soaking alone is not a dominant stress factor. A dramatic improvement in UV-stability has been reached by using MgI_2 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 are now obtained for cells based on pure nitrile based solvents. 1) a minor decrease of performance of initially 5% solar efficient cells has been found after 2000 h at 60 °C storage in the dark. 2) After 3400 hours of combined thermal stress and continuous light soaking (45 °C, 1 sun equiv.) good stability with 15 % decrease in maximum power could be demonstrated.

Keywords: Solar Cell-1: Dye sensitisation-2: Stability-3:

1. INTRODUCTION

1.1 Overview

Nanocrystalline dye sensitised solar cells (nc-DSC) developed by Grätzel et al. [1] have achieved solar power efficiencies up to 10 % on small areas [2]. The cells consist of a thin film of porous nanocrystalline TiO_2 coated with a ruthenium metal organic dye to absorb the light energy. Photoexcitation of the dye leads to injection of electrons in the conduction band of the oxide. The oxidised dye accepts electrons from iodide ions present in the electrolyte and the resulting tri-iodide ions are reduced back to I^- at the platinum coated counter electrode.

For a successful introduction of nc-DSC for outdoor applications, specifically for large area power applications, several factors are of importance, among others: technical performance and manufacturability, costs, design, market demand and last but not least the long term stability.

The overall stability of this cell is controlled by two factors, namely the physical and chemical stability. The physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technologically related problem, for which solutions should be found by using suitable sealing materials and techniques. The intrinsic chemical stability is related to irreversible (photo-) electrochemical and thermal degradation of the dye or electrolyte components, which can occur during electrical operation of the cell.

Previous long-term stability tests on low-efficiency nc-DSCs sealed with polymer adhesives [3] demonstrated no significant decrease of the performance over a period of 10.000 hours under continuous 1 sun illumination.

1.2 Aims of current project

ECN, INAP Gelsenkirchen, FMF Freiburg and Solaronix collaborate in the framework of the EU-project LOTS-DSC, which focuses mainly on the chemical

stability issues of the nc-DSC. In addition, efficiency is addressed in this project, since it is essential to investigate the stability of highly efficient devices. The main objective of this project is to demonstrate that a 10 year outdoor module lifetime is feasible

1.3 Approach

In order to reach this goal within a project period of three years, it is of importance to develop appropriate accelerated ageing test procedures for nc-DSC so that useful extrapolations to real outdoor conditions can be made. Several stress factors can be distinguished and are applied to the DSC:

1. Light
 - 1.1. Visible light
 - 1.2 UV-light
2. Temperature
3. Electrical operation mode of the DSC under illumination (open circuit, short circuit)

In this paper we describe our encouraging results gained from these stability tests thus far. Also, we discuss the degradation mechanisms involved and present possible steps for further optimisation.

2. EXPERIMENTAL

2.1 Measurement objects, master plates

The nc-DSCs for the stability tests are fabricated on so called masterplates. These plates consist of five individual cells of $5 \times 0.8 \text{ cm}^2$ on a $SnO_2:F$ -glass substrate (LOF 8 Ohm/square). TiO_2 layers are deposited by using the screen printing technique. A silver strip on each side of the cell ensures proper current collection within the masterplate. Pt coated $SnO_2:F$ substrates were used as the counter electrodes. Surllyn 1702 (Dupont) is used as the primary sealing material. A representative picture of a

masterplate during fabrication is shown in figure 1. In total, more than 100 masterplates have been manufactured in this manner, thus far. The sensitising dye used for the masterplates was *cis*-di(thiocyanato)-*N,N'*-bis(2,2''bi pyridyl-4,4'-dicarboxylate)Ru(II) (N3) or its two-fold deprotonated form (N719).

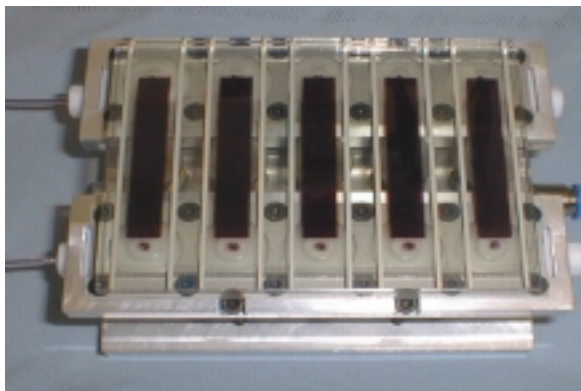


Figure 1: Processing of a master plate (75 mm x 100 mm) containing 5 individual dye sensitised test cells (active area 4 cm²). The coloration step, flushing of dye solution after sealing through holes on a filling unit, is shown.

This concept was chosen in order to be able to obtain reproducible results, which is a necessity in the study of small effects that results from stability tests. In table 1, efficiency data of two different masterplates are presented. The results indicate that for all measured photovoltaic parameters the reproducibility for 5 cells on one masterplate can indeed be achieved within 10 %.

Table 1: Table with reproducibility efficiency of two masterplates

Masterplate cell number	J _{sc} mA·cm ⁻²	U _{oc} V	FF %	Efficiency % @1000W/m ²
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

2.2 Characterisation and ageing

Continuous strong light soaking and on-line characterisation of the photovoltaic parameters is done in identical sites (figure 2) at the partners. For a long-term stable light source sulphur plasma lamps are used. The sulphur lamp spectrum is continuous from 400 nm to 800 nm with its maximum at 500 nm, matching very well the spectral sensitivity of the dye sensitised solar cells. Si-reference cells control the lamp intensity. The cell temperature in the light soaking sites can be varied.

Every week, the cells are automatically characterised in the illumination sites and the data is electronically

transferred to a central database at FMF Freiburg. In order to manage the large amounts of data, MS SQL-Server as DBMS (database management system) is used.



Figure 2: Photos of continuous illumination and characterisation sites for simultaneous light soaking experiments. At each site 16 master plates 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.

UV-ageing is done in two sites using densely packed UV-light emitting fluorescence tubes (UV-TLK40/05). The UV-lamp spectrum is continuous, reaching from 345 nm to 400 nm and matching perfectly the photoactivity spectrum of TiO₂ in the cell. The UV-intensity is 10 mW/cm² at the sample area. The cell temperature is kept constant at 20 °C.

Electrical impedance spectroscopy (EIS) [8] is done with an IM6 potentiostat from Zahner electric.

Degradation products in the electrolyte are detected by gas chromatography - mass spectroscopic method (GC-MS).

3. RESULTS

3.1 Light soaking at room temperature

Before the LOTS-DSC project started, preliminary stability studies were done on low efficiency (ca. 2 %) single cells. In figure 3 the best results from long-term (8300 h) light soaking experiments (single cell measurements) are shown [4]. The cell temperature under strong visible light illumination was 20 °C in order to avoid thermal stress. The photon flux absorbed by the cells during illumination was equivalent to the effect under 2.5 sun illumination excluding the UV-part. There is a small decrease (50 mV) in open circuit voltage after exposure, which is compensated by the increase in short circuit current.

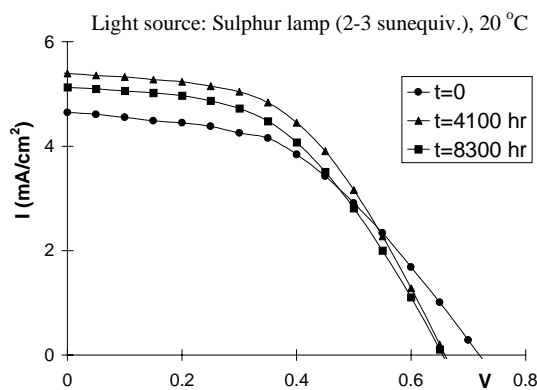


Figure 3: Current-voltage curves for low efficiency (2%) nc-DSC single cell under continuous 2.5 sun equivalent illumination. Cell makeup: Dye: N3, TiO₂: P25, electrolyte: 0.4 M HMII (hexyl-methyl-imidazolium iodide), 0.1 M LiI, 0.05 M I₂, 0.3 M TBP (tert-butyl-pyridine) in methoxypropionitrile. The I-V measurements were taken under class A solar simulator (1000 W/m²) without spectral mismatch correction.

3.2 Testing under UV-light

Exposure to UV-light has been found to be deterring for some nc-DSC. Electrolyte additives can cause large differences in UV-light stability. The effect of addition of MgI₂ to the electrolyte was studied for single cells after ageing with UV-light. As can be clearly seen from figure 4, MgI₂ has a stabilising effect on the UV-stability of the tested nc-DSC. On the other hand, addition of MgI₂ leads to a significant decrease of the V_{oc}.

The influence of other additives like CaI₂ and 2-Phenylimidazole in various electrolyte compositions have been studied and some of these results are shown in figure 5. It can be seen that both MgI₂ and CaI₂ show strong UV-stabilising effects.

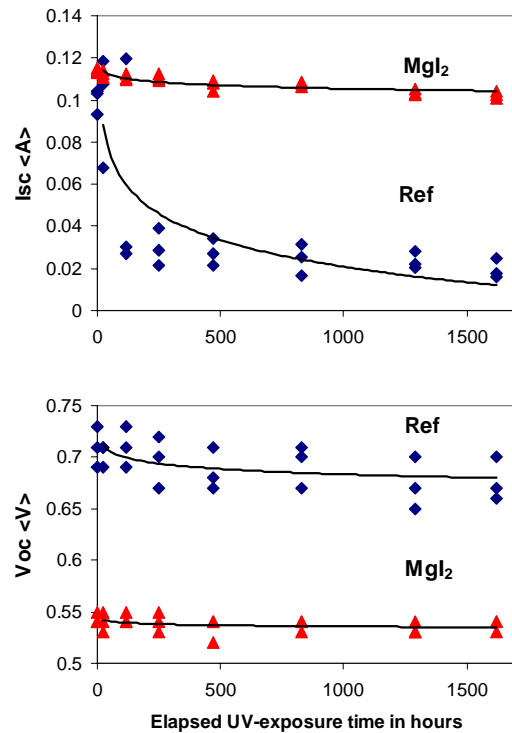


Figure 4: UV-stability of cells in V_{oc} and I_{sc} with and without MgI₂ electrolyte additive. Cell area in this case 7.5 cm x 1.5 cm. Electrolyte: 0.3 M HMII, 30 mM I₂, 0.6 M TBP, 0.5 M MgI₂ in CH₃CN. Reference without MgI₂.

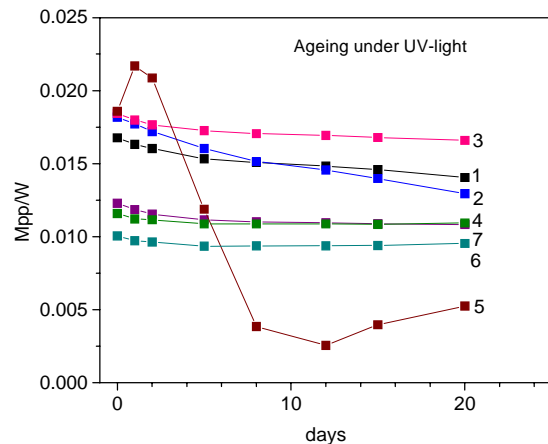


Figure 5: Stability data (maximum power point) of cells on masterplates after ageing with a UV-light tester (cell temperature 35 °C). Electrolyte no. 5 is the (unstable) reference without additive. Electrolytes:

- 1- 0.5 M MgI₂, 0.3 M HMII, 0.6 M TBP, 30 mM I₂,
 - 2- 0.5 M MgI₂, 0.3 M HMII, 2.5 M TBP, 30 mM I₂,
 - 3- 0.2 M CaI₂aq, 0.4 M HMII, 40 mM I₂, 1.3 M TBP,
 - 4- 0.6 M CaI₂aq, 0.3 M HMII, 40 mM I₂, 1.3 M TBP,
 - 5- 0.5 M HMII, 40 mM I₂, 0.7 M TBP,
 - 6- 0.2 M. CaI₂aq, 50 mM I₂, 0.42 M 2-Phenylimidazole
 - 7- 0.2 M. CaI₂aq, 0.5 M HMII, 50 mM I₂, 0.42 M 2-Phenylimidazole;
- solvent in all cases CH₃CN.

3.3 Light soaking at elevated temperatures

Since the start of the project more than 50 masterplates were already exposed to the sulphur lamp in the stability test stands. The light intensity was adjusted to approximately 1 sun while the temperature was around 45 °C. The first stability results that were obtained from these tests show some striking differences in stability when different electrolyte solvents are used. For instance, cells containing methoxyacetonitril show poor stability behavior, while propionitril seems to be a proper choice for further research. In general, a very small decrease of I_{sc} and a gradual decrease of V_{oc} over time is observed.

A typical example is shown in figure 6, where after 3400 h of ageing, a decrease in maximum power of less than 15% has been reached.

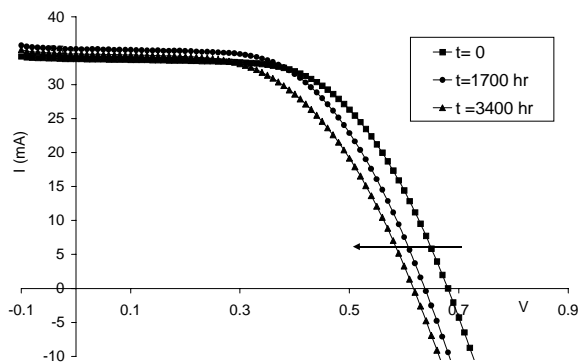


Figure 6: Results from 1 sun equivalent light soaking at 45 °C, Electrolyte: 0.6 M HMII, 0.1 M LiI, 0.05 M I₂, 0.5 M TBP in propionitril (chemicals used as received)

3.4 Thermal ageing

In order to examine the influence of the temperature on the long term stability of nc-DSC, masterplates are aged in ovens at different temperatures without light soaking. For cells containing methoxyacetonitril as the electrolyte solvent strong degradation of the performance was observed.

In order to examine the origin of these degradations, the chemical composition of the aged electrolyte was analysed with GC-MS. The results are compiled in figure 7. From the analyses it was found that methoxyacetamid (via hydrolysis of methoxyacetonitril) was formed after ageing.

As can be seen in the figure the amount of methoxyacetamid is strongly dependent on the storage temperature. Furthermore methoxyacetamid was not detected in the electrolyte reference and only formed in the solar cell (even after storage at 7 degrees !). In further experiments the influence of this specific degradation product on the cell stability will be investigated.

In order to find physical explanations for the degradation behaviour, more physical characterisation methods are needed. Electrical impedance spectroscopy (EIS) has shown to be a useful technique for the extraction of parameters determining the behaviour of DSC. Observed changes in the EIS of DSC after ageing can lead to a better understanding of the degradation phenomena of the cells.

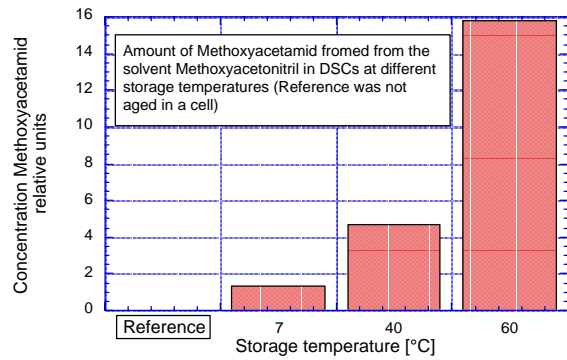


Figure 7. Relative amount of methoxyacetamide as analysed with GC-MS in electrolyte after thermal stress test at 7, 40 and 60 °C.

In Figure 8 EIS spectra are shown of a thermally unstable cell based on methoxyacetonitril. Ageing has been carried out at 60 °C up to 435 h in the dark. The magnitude of the EIS in open circuit under 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 free photoelectrons in the TiO₂ conduction band [5]. As is observed in Table 2, a correlation exists between I_{sc} and the main peak frequency F_{max} of the EIS measurement.

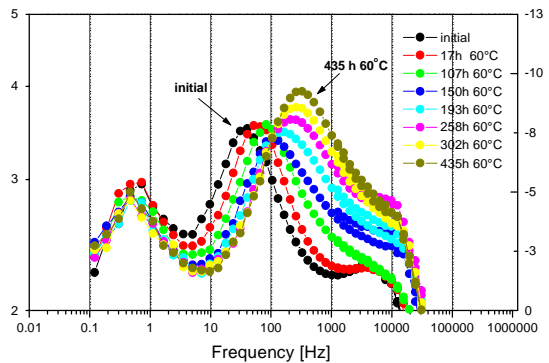


Figure 8: EIS (phase) on cells containing methoxyacetonitrile aged at 60 °C up to 435 hours in the dark.

Table 2: Correlation between short circuit current I_{sc} and main peak frequency F_{max} of the EIS measurement in figure 8 for cells tempered in the dark.

Time	Cell 450 kept at 7°C		Cell 465 aged at 40°C		Cell 470 aged at 60°C	
	I _{sc} mA	F _{max} Hz	I _{sc} mA	F _{max} Hz	I _{sc} mA	F _{max} Hz
0	43	26	49	26	46	33
17 h	-	-	47	26	41	43
107 h	41	26	45	26	32	69
150 h	44	26	46	26	28	87
193 h	42	26	42	33	26	137
258 h	42	26	41	33	22	200
302 h	44	26	41	33	21	216
435 h	44	26	39	33	20	270

The best result of a thermal stress test at 60 °C achieved thus far is shown in figure 9 for cells containing propionitril as the electrolyte solvent. Nearly no decrease in cell efficiency after 2000 h is observed which is a very encouraging result. It should be realised that these tests require reliable and stable sealing materials in order to prevent leakage of the solvent.

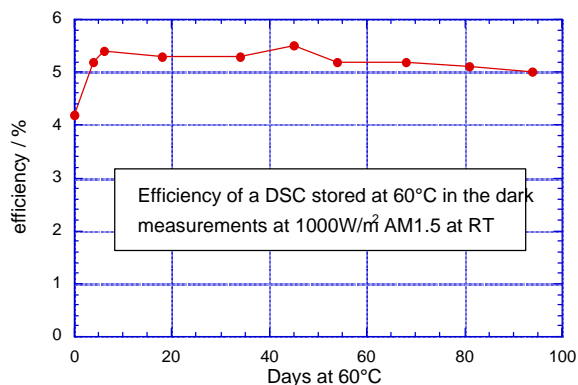


Figure 9: Best results achieved so far with thermal ageing in the dark. Electrolyte is based on dimethyl propyl imidazoilium iodide (DMPII), LiI, I₂, TBP and propionitril. All the chemicals were purified before use.

4. DISCUSSION

4.1 Photo-electrochemical stability

Intense visible light soaking (“2.5 sun” sulphur lamp) alone is not a dominant stress factor for dye sensitised solar cells (figure 3). Remarkably, as predicted already in the “early” days [1] and doubted by many, the system is very regenerative in terms of photo-electrochemical stability (amount of turnovers). As explanation, the following hypothesis has been proposed [6]; the photo-excited state of the dye is very rapidly (sub pico-seconds) quenched by electron transfer to the titanium dioxide. The oxidised dye molecules (Ruthenium (III) centre) are then quickly enough regenerated (reduced) by iodide from the redox couple in the electrolyte to prevent non-regenerative side reactions.

There are also hypotheses that would predict degradation under visible light [7]. One is, that always a small fraction of dye molecules will not be attached strongly enough 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⁻ ligands from the dye with the iodide ion or water during the lifetime of the excited state [3]. Why such mechanisms have seemingly no large effect on stability of dye sensitised solar cells under visible light stress, is not yet fully understood.

4.2 Direct band-gap excitation under UV

UV- light has in many cases 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 concentration, is irreversibly consumed (bleached) under UV-light illumination. As iodine is necessary in the redox pair I/I₂, the electrolyte in

this case becomes electrochemically blocking at the counter electrode side. The explanation for the bleaching of the iodine can be side reactions of the photo-generated 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.

4.3 UV-stabilisation of electrolyte using MgI₂

Besides the option to apply UV-filters (foils) as protection against UV-light, our results demonstrate that certain electrolyte additives can dramatically increase the UV-stability (2000 hours). The most effective additive found so far is MgI₂ (figure 4). As is indicated from the lower photovoltage, Mg²⁺ is charging the TiO₂ surface more positive. Fortunately as demonstrated in figure 5, this effect can be compensated by enhancing the amount of tert-butyl-pyridine in the electrolyte without loss in photocurrent. It should also be noted, that MgI₂ seems not to block the hole reactions at the titanium dioxide surface, uncoloured photoelectrodes show a good photocurrent under UV-light caused by direct band-gap excitation of the TiO₂. There are several explanations possible for the enhanced stability, a faster reduction of the holes by iodine, the lower photopotential, and the formation of a MgO surface layer preventing side reactions. CaI₂ seemingly also has an UV-stabilising effect (figure 5) and it requires less tert-butyl-pyridine base additive to compensate for the drop in voltage than in the case of MgI₂.

4.4 UV-stability of the dye

As can be concluded from the stable photocurrent under UV-light illumination for cells containing MgI₂, the dye itself seems not to be attacked by the UV-light. This is quite striking, because free R-COOH groups similar to the attachment groups of the dye are known in literature 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. There might be therefore also stabilising mechanisms under UV-light illumination, which we do not know. One possible mechanism to be considered for capturing the photo-oxidative electron vacancy (hole) at the TiO₂ surface is the reversible oxidation of the Ru(II) –center of the dye.

4.5 Electrolyte solvent

Another unwanted side reaction to be considered under UV-illumination is the photooxidation of the electrolyte solvents. This is forcing us up-to-now to use UV-stable, but rather toxic nitriles as electrolyte solvents. More electrolyte solvents have to be scanned in further experiments also in combination with effective UV-stabilising additives like MgI₂.

4.6 Thermal activation energies

The thermal stability is the most critical item. At least a single-exponential response in degradation rate to the 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 a required thermal stress 80 °C, 1000 h should at least be targeted for mid-European locations. This would correspond to 20 days, 5 hours 80 °C per year over 10 years. Up-to-now 2000 h at 60 °C stability have been demonstrated (figure 7) for cells having 5% solar efficiency.. These results are very promising, but still not enough to state enough about thermal activation energies.

4.7 Catalytic reactions

It should not be forgotten that two catalysts (TiO₂ 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 pair catalytic reactions are quenched, but to which extent is not known. Especially in the case of the TiO₂ a correlation between amount of catalyst, i.e. the layer thickness, and the thermal stability can be expected.

4.8 Chemical nature of electrolyte solvent

Another point is the chemical nature of the electrolyte solvent and its possible decomposition products and reaction routes with the electrolyte components under thermal stress. Also in this case, experience has shown so far, that pure nitrile based solvent (acetonitrile, propionitrile) are most stable. Solvents containing chemically bonded oxygen are tested as much less stable so far. It was described in section 3.3 that after thermal aging of cells containing methoxyacetonitril, methoxyacetamide was found as a degradation product. Residues of water in the solvent and on the TiO₂ surface have probably caused this hydrolysis reaction. Never-the-less, solvents containing N-C=O bonds like 1-Methyl-2-pyrrolidone (NMP) which are far less toxic should be tested (again). Very contradictory results have been seen so far with gamma-butyrolactone. A crucial item to answer these questions in further experiments is therefore the purity of the solvent and the inert handling during cell manufacturing.

4.9 Permeability of sealing material

Under thermal stress above 60 °C, the permeability of the sealing material towards solvent, oxygen and humidity can become an important item, which can interfere with the “internal” chemical stability. The influence of oxygen on stability measurements can easily be excluded by thermally ageing of the master plates in an inert atmosphere (N₂). As a reference at higher temperature, cells that have been sealed by glass frit techniques or higher melting hotmelt foils will be aged in further experiments.

4.10 Short circuit current after thermal stress

Hypotheses for the decrease in short circuit current after thermal stress are:

- The reduction of the electron diffusion length in the titanium dioxide because of surface modifications (traps), weakening of the inter-particle connections, or even changes in the TiO₂ crystal structure. In these cases, the electron remains trapped longer inside the titanium dioxide (or at the surface) which enhances the probability for recombination with I₂ in the electrolyte. As this process takes place at the photoelectrode side and not at the counter, it can be seen as internal recombination resulting in a loss of external photocurrent. To first order, the external photovoltage is not effected. The observations done

by EIS and reported in table 2 strengthen this hypothesis.

- Reduction of the electron injection efficiency of the dye or changes in the dye absorption spectra (replacement of ligands).
- Side products in the aged electrolyte which quench (reduce) the oxidized dye state and are in concurrence with the iodide / I₂ reaction. These products are most likely longer living radicals which also are recombining (regenerating) with the iodide, but in time scales (sec) which are longer then those (10 ms) required for an efficient charge transport under full sun illumination. +
- Decomposition products in the electrolyte co-adsorbing to the TiO₂ surface and causing partial desorption of the dye.
- Diffusion of platinum from the counter electrode to the TiO₂ and/or TCO surface. As a result an enhanced internal recombination current is expected.

4.11 Open circuit voltage after thermal stress

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

- Release of protons (acid formation) from the electrolyte solvent. In this case, a “pH-buffer” like tert-butyl pyridine might be advantageous.
- Diffusion of platinum to the TCO (SnO₂:F) surface resulting in a higher dark current and therefore lower open circuit voltage
- Formation of other side products on the TCO interface. In both cases a thin under layer of TiO₂ on the TCO might be advantageous.
- More general it might well be, that thermal induced changes at the TCO interface have a stronger influence on V_{oc}, than in the case of the TiO₂ electrode layer.

5. CONCLUSIONS

Our accelerated ageing tests on large numbers of dye sensitised solar cells show, that to first order a separation between the effects of the stresses visible light soaking, UV-illumination and thermal treatment on long-term stability can be made. The corresponding mechanisms are of electrochemical, photochemical and pure chemical nature respectively.

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 corresponding to at least 10 years outdoor equivalent operation.

Very successful are our results on UV-stabilisation. A dramatic improvement in stability under strong UV-light illumination has been reached by using MgI₂ as additive to the electrolyte. 1600 h under this condition have been demonstrated corresponding to at least 2 year outdoor equivalent operation without (!) additional UV-filter. In combination with a simple UV-filtering top-layer, dye sensitised solar cells can therefore be UV-stabilised for real (10 year) long-term outdoor operation.

The long-term extrapolation of the thermal stability achieved so far is still most critical. Experiments at higher

temperatures (80 °C to 100 °C) have still to be made to learn more about thermal activation energies. Also, the upper module temperatures in outdoor condition of DSCs depending on location and module mounting (roof, stand-alone, facade) have to be determined. Nevertheless, the results (minor decrease from 5% solar efficient cells after 2000 h at 60 °C in the dark) are very promising.

For cells under combined thermal stress and light soaking (3400 h, 45 °C) so far good stability with 15 % decrease in maximum power could be demonstrated. Under certain outdoor conditions a first extrapolation to 5 year stability can be drawn from these results.

Not studied so far has been the effect of applying periodic stresses. Physical failures but also healing effects are expected then.

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 the chemical balancing of the electrolyte components. The on-going work will therefore focus especially on the chemical part on a device level.

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