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Long-term stability testing of dye-sensitized solar cells

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Abstract

This study comprises the behavior of dye-sensitized nanocrystalline TiO_2 solar cells (nc-DSC) under various testing conditions regarding accelerated aging. nc-DSCs are potentially vulnerable to various kinds of degradation. The cell performance is seriously decreased upon heat treatments, despite the fact that leakage of the electrolyte liquid is effectively prevented. Even when cells are stored in the dark at elevated temperatures, apparently side reactions occur, resulting in cell degradation.

Since elevated temperatures are hard to exclude under normal operation conditions, this is the most critical criterion regarding long-term stability. The nc-DSC should be modified in such a way that it is not sensitive to elevated temperatures, representative for outdoor conditions. The emphasis of this paper is on the long-term stability of nc-DSCs at high temperature. nc-DSCs have been subjected to various aging tests. A cyclic test comprising thermal stress in the dark (85 °C) alternated by full sun illumination under milder conditions reveals a recovery process occurring in degraded cells. A combination of 85 °C and full sun illumination leads to a significant decrease of the cell performance.

Keywords: Dye-sensitized; Stability; TiO_2

1. Introduction

The dye-sensitized solar cell, based on dye-sensitized nanocrystalline titanium dioxide that has been developed by Grätzel and coworkers [1,2] has attracted a lot of interest since its discovery. Remarkably high quantum efficiencies have been reported for this type of solar cell (nc-DSC), with overall conversion efficiencies up to 11% for small surface areas ($<1\,cm^2$) [3]. This fact, in combination with the expected relative ease and low cost of manufacturing makes this new technology an interesting alternative for existing solar cell technologies based on silicon.

Realization of stable efficiencies in the order of 10% in production, however, requires a lot of effort in research and development. Considering the cell efficiency, technological improvements have led to a better reproducibility and higher efficiencies on surface areas of at least $1\,cm^2$ [4–7]. Moreover cell efficiency values have been translated from $4\,cm^2$ cells to $100\,cm^2$ devices [4], representing a cell with a realistic size for industrial processing.

The long-term stability of the nc-DSC system has been subject of concern during the past years of development of this technology. The nc-DSC are potentially vulnerable to various kinds of degradations:

1. The system contains an organic liquid which can leak out of the cell or evaporate at elevated temperatures. In principle this can be overcome by using appropriate sealing materials.
2. A potential problem comprises the titanium dioxide. TiO_2 is an efficient photocatalyst, putting at risk the organic materials (dye, electrolyte solvent) in its direct vicinity under natural illumination (including UV light). UV light can lead to direct band gap excitation of the TiO_2 and subsequent oxidation of the dye or the electrolyte components. The kinetics of these and other possible side reactions in a complete cell are however slow compared to the normal processes of operation, preventing degradation. If this is not sufficient, application of a UV filter is an effective method to solve this problem.
3. A less expected mode of degradation can occur at high temperatures. Apart from the risk of evaporation of the electrolyte solvent, a high temperature can induce a decrease of the nc-DSC performance, depending on the cell composition. This is an intrinsic stability issue, i.e. this degradation also occurs in perfectly sealed devices and cannot be prevented by external techniques like application of filters.

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In the past, application of volatile solvents in the electrolyte in combination with imperfect sealing frequently resulted in leakage and evaporation of electrolyte at elevated temperatures. This masked intrinsic chemical degradation at elevated temperatures, if any. The problem could be relieved by application of solvents with higher boiling points or ionic liquids as a basis for the electrolyte. Kohle et al. [8] reported on cells containing a solvent with a high boiling point, glutarodinitrile. The cell efficiency was low (1%) due to the high viscosity of the solvent. No decrease in cell performance was observed after 7000 h of simulated solar light at full sun intensity (approximately room temperature). Other studies [9,10] revealed a slight decrease of V_{oc} after 8000 h of continuous illumination at 1 sun equivalent at room temperature, which was compensated by an increase in I_{sc}. These results revealed that the applied ruthenium dye (N3 or N719) is capable of making many turnovers (more than 10^7) in the given chemical environment without degradation at or near room temperature. This means that light soaking, i.e. a high photon flux as such, is not a dominant stress factor. It also shows that the kinetics of the fundamental chemical processes in the cell are tuned in such a way that undesired side reactions (for example oxidation of the excited state of the dye) are effectively suppressed.

In practice, however, solar modules for outdoor applications are subject to more extreme conditions than full sun irradiation alone. Accelerated aging tests were performed on a large number (>500) of encapsulated monolithic nc-DSC modules for low power indoor applications [11]. An important factor is thermal stress caused by heating and cooling in a day/night cycle. Apart from leakage or evaporation of solvent, thermal stress can cause intrinsic chemical degradation. To qualify the packaging and mechanical integrity of solar modules, accelerated aging test procedures have been developed [9,12] based on standard test conditions required for thin film and crystalline silicon modules (IEC 1646:1996 and IEC 1215:1993). Applying IEC tests at ECN, like thermal annealing at 85 °C and a damp heat test at 85 °C, positive results were obtained as far as the packaging quality of the nc-DSCs was concerned (unpublished) for devices sealed with polymer hot melts. Devices with improved sealants, filled with volatile solvents like acetonitrile, are able to withstand temperatures of 85 °C for a prolonged time without leakage of the electrolyte. However, considering the intrinsic cell stability, thermal annealing at 85 °C turns out to be a major stress factor for nc-DSCs. Rapid chemical degradation occurs despite improved sealing materials (high temperature hot melts or glass frits) [9]. This can be due to inherent chemical side reactions between different cell ingredients, but also impurities present in chemicals or related to processing (humidity) can play a role here. For this reason it is very hard to compare results from different laboratories in this field and at present these results should be considered as laboratory specific, i.e. not valid in general.

Recently a new derivative of the ruthenium N719 dye has been developed, exhibiting a major improvement in cell properties regarding the resistance towards thermal stress [13]. Applying this dye (Z 907, substitution of long alkyl chains to the bipyridyl ligand renders the molecule hydrophobic) it is possible for a nc-DSC to withstand continuous heating at 85 °C for a period of 1000 h and visible light soaking at 55 °C during 1000 h. Though this result is very promising in itself one has to be aware of the fact that this test does not reflect a realistic outdoor condition, i.e. 85 °C in the dark is not a natural circumstance. Only in combination with high light intensities these high temperatures can be reached. On the other hand, since this test is a part of the current IEC testing sequence for thin film and crystalline silicon modules, it is still a relevant test.

In this paper a more detailed study is made of the response of the nc-DSC system towards different testing (both realistic and artificial) conditions. Cells have been exposed to thermal stress both in the dark and under full sun illumination and to a cyclic test comprising thermal stress in the dark alternated by full sun illumination under milder conditions. The response of cells based on various electrolyte compositions has been investigated. Other cell components (such as dye, Pt, TiO_2) have been kept equal for all cells involved in this study.

2. Experimental

2.1. Cell preparation

Preparation of TiO_2 colloids and screen printable paste has been carried out according to procedures described elsewhere [14]. In short, titaniumisopropoxide is hydrolyzed in water. After peptization at 80 °C, a colloidal TiO_2 solution is obtained, containing TiO_2 particles with a size in the range of a few nanometer. To obtain TiO_2 particles of a desired size, a hydrothermal growth process is conducted in an autoclave, resulting in particle sizes between 20 and 40 nm depending on conditions. The TiO_2 colloid is transferred from the aqueous solution into a terpineol/ethylcellulose mixture to obtain a screen printable paste using a pearl mill.

N719 dye has been purchased from Solaronix S.A. in Switzerland. Electrolyte solvents and additives (*N*-methylbenzimidazole (NMBI), hexylmethylimidazolium iodide (HMI), butylmethylimidazoliumiodide (BMI), dimethylpropylimidazolium iodide (DMPI), *tert*-butyl pyridine (TBP), lithium iodide (LiI) (Aldrich)) have been used as received without purification.

Master plates have been applied as a research vehicle. A master plate consists of two glass plates (7.5 cm × 10 cm) on which five electrically isolated electrodes are deposited by screen printing (Fig. 1). One glass plate contains five photoelectrodes, the other contains five counter electrodes. The active layers (TiO_2 and Pt) are dried and fired at 450 °C to remove all organic components and to establish sufficient inter-particle contacts between the TiO_2 particles. A typical film thickness of 10 μm results after firing. The two glass plates comprising the photo and counter electrodes

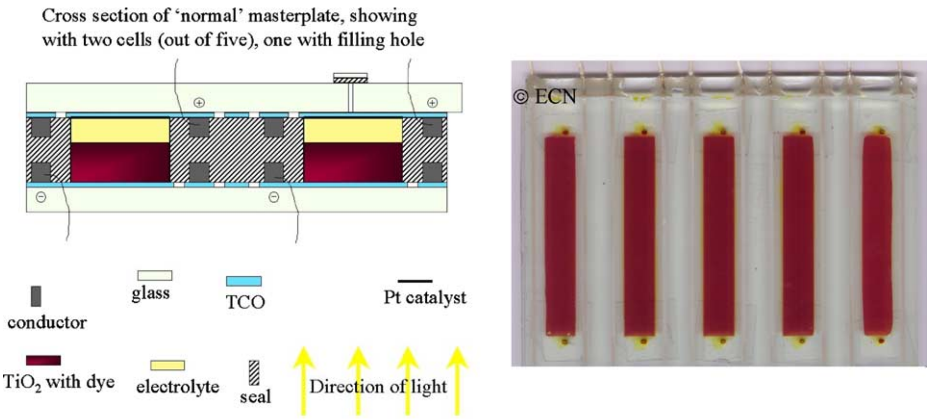

Fig. 1. Master plate and cross-section.

are laminated together using hotmelt foils like surlyn or bynel.

In the next step the TiO_2 films are colored by means of a specially developed coloration machine that is able to pump a dye solution through the five cell compartments, using two holes present in the counter electrode of each cell compartment. Coloration parameters like temperature, time and concentrations can be carefully controlled in this way. After completion of the coloration the cell compartments are flushed with acetonitrile, dried with nitrogen and filled with electrolyte. Finally, the filling holes in the counter electrodes are closed with hotmelt foil and a glass plate, creating five individual cells in one unit. An advantage of the master plate concept over individual cells is the reproducibility of the five cells on each plate, because by definition all processing steps up to the filling are exactly equal for all five cells. This makes the master plate very suitable for studying the influence of different electrolyte compositions. In this study for every master plate three different electrolytes have been applied, keeping all other cell components, processing and testing conditions equal for five cells.

The following electrolyte compositions have been used in the master plates:

- EL 1: 0.6 M BMI, 0.1 M LiI, 0.05 M I_2 and 0.5 M TBP in a mixture of acetonitrile/valeronitrile (85/15 v/v);
- EL 2: 0.6 M HMI, 0.1 M LiI, 0.05 M I_2 and 0.5 M TBP in acetonitrile;
- EL 3: 0.6 M DMPI, 0.1 M I_2 and 0.5 M NMBI in acetonitrile.

2.2. Cell aging tests

Master plates comprising cells with various electrolyte compositions have been subjected to different kinds of aging tests:

1. Visible light soaking: constant illumination at 45 °C under 1 sun artificial illumination under a sulfur lamp setup [9].
2. Thermal annealing/illumination cycling: dark heating at 85 °C in an oven (Heraeus) alternated by 1 sun illumination at 45 °C.
3. Thermal annealing/illumination combined: constant heating at 85 °C in combination with constant artificial 1 sun illumination at one time.

The solar cells have been in open circuit during the aging tests. Test no. 3 mimics a worst case realistic situation, using the sulfur lamp and a thermostatic hot plate. During this test the cells have been kept in maximum power point. As a reference, master plates with equal cell compositions have been stored in the dark at room temperature.

IV measurements have been carried out offline (cells were taken out of the testing equipment) at room temperature using a Steuernagel constant 575 solar simulator.

3. Results and discussion

3.1. Visible light soaking

Under illumination of approximately 1 sun at moderate temperatures (45 °C) a minor decrease in cell performance is shown, comparable to test results under full sun illumination at room temperature, as reported earlier [9]. In this study master plates have been tested under a relatively mild test, involving 1 sun illumination at 45 °C, as a reference for comparison to the other degradation tests described in Section 2.2. No major changes in short circuit currents occur during the period of testing (approximately 1200 h) (Fig. 2), although the decrease in V_{oc} for these cells during this test is approximately 10%, resulting in an overall decrease in efficiency of 12–15%.

3.2. Thermal annealing/illumination cycling

Fig. 3 represents the changes in *IV* parameters as a result of various test conditions. In the first 110 h the cells have been stored in the dark at 85 °C resulting in a dramatic drop

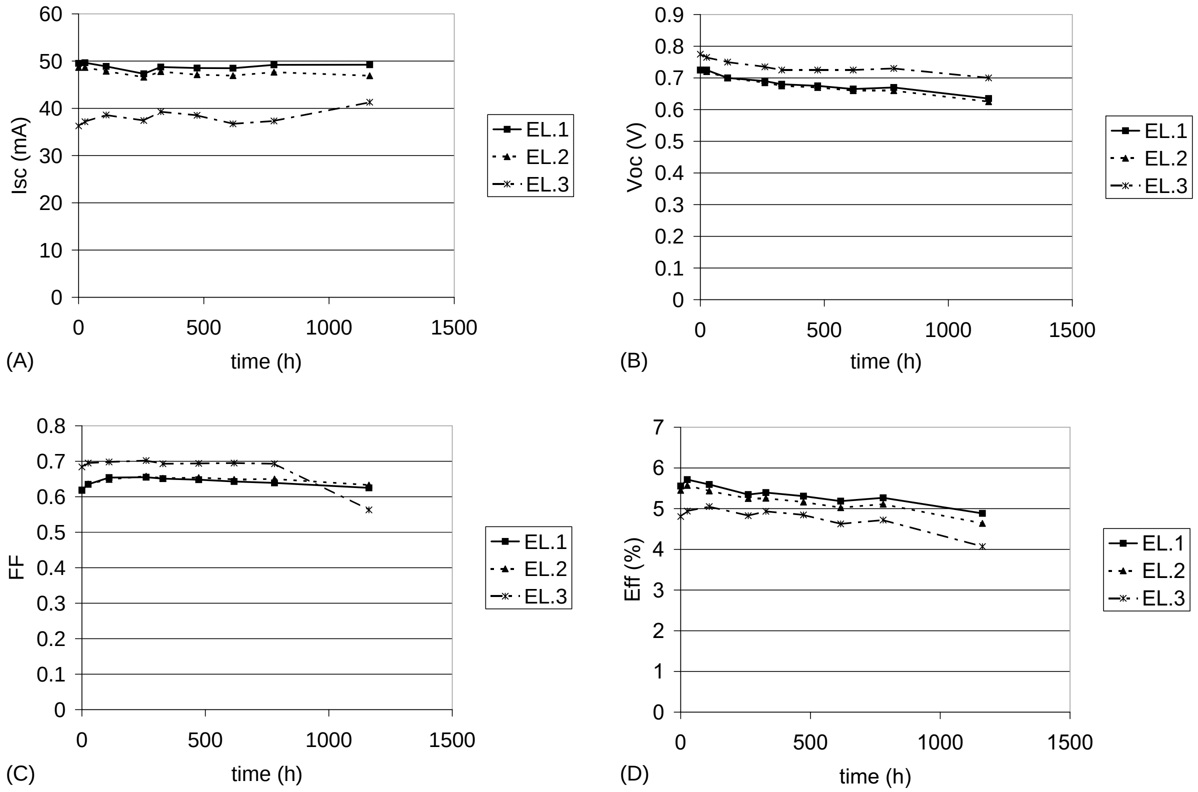

Fig. 2. Stability data for three cells during constant illumination at approximately 1 sun and 45 °C: (A) I_{sc}; (B) V_{oc}; (C) FF; (D) Eff.

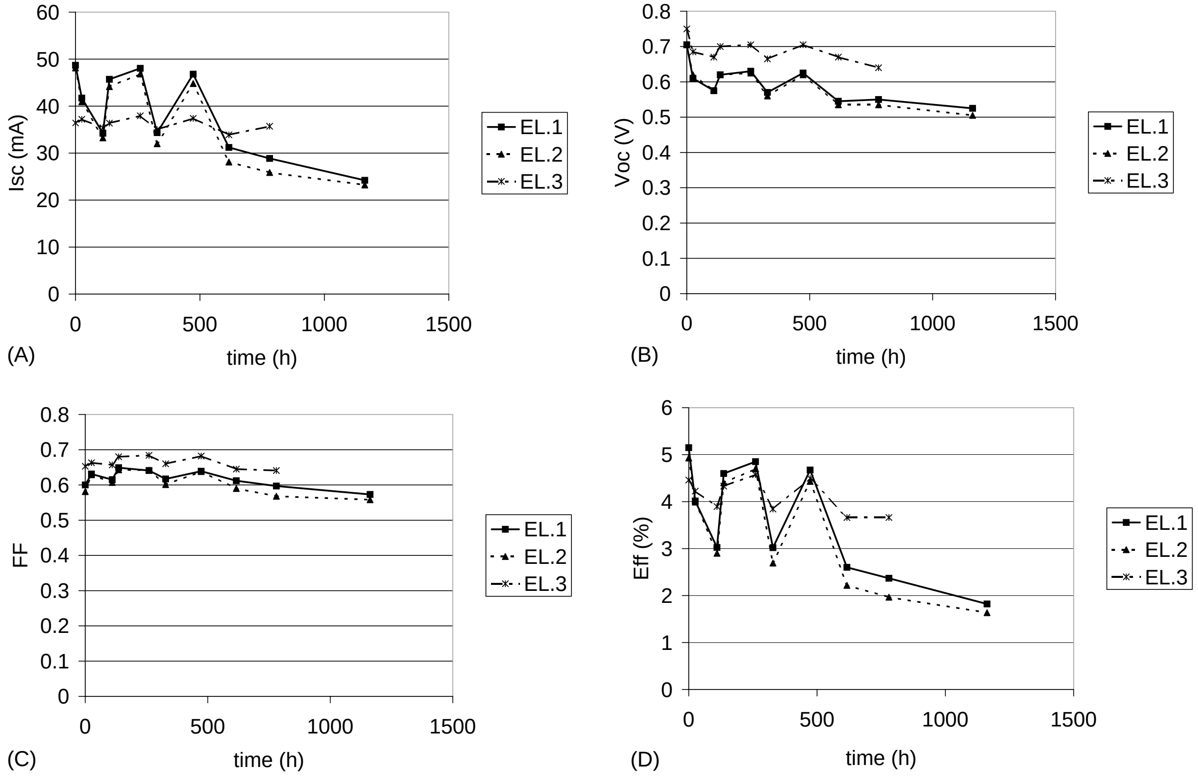

Fig. 3. Stability data for three cells depending on conditions—from 0 to 110, 260 to 328 and 473 to 1162 h: 85 °C, dark; from 110 to 260 and 328 to 473 h: 45 °C, 1 sun. Note: cell filled with EL 3 started leaking around 800 h: (A) I_{sc}; (B) V_{oc}; (C) FF; (D) Eff.

in I_{sc}. V_{oc} and FF are also lowered. For electrolyte EL 3 the effect is less severe than for EL 1 and 2.

This is different from the result in the visible light-soaking test. As has been reported earlier [9] elevated temperatures can result in a decrease of cell performance, depending on the temperature. At 60 °C a constant power output during 1000 h was demonstrated. At 85 °C, however, a serious degradation occurs, indicating an activation-controlled process. It should be noted that leakage of electrolyte solvent does not play a role in this degradation. The study of [9] involved glass sealed devices, so evaporation or leakage of solvent was effectively prevented.

From Fig. 3 it can be derived that the initial decrease in performance at 85 °C is reversible. Switching the testing conditions from 85 °C/dark, to 45 °C/1 sun illumination results in a recovery of the cell performance (Fig. 3, from 110 to 260 h). After 110 h at 85 °C/dark the cell efficiency is decreased to 59% of the initial value for cells filled with electrolyte EL 1. A spectacular recovery to 89% of the initial value after 26 h under 45 °C/1 sun occurs, increasing to 94% after an extra 124 h under 45 °C/1 sun. After a second cycle of degradation in the dark at 85 °C the performance recovers again during illumination at 45 °C. To address the influence of illumination on this recovery process another master plate has been stored in the dark after the second degradation cycle at 85 °C (260–328 h).

As can be derived by comparing the Figs. 3 and 4 (starting at 328 h) it appears that the recovery is strongly enhanced by illumination at 45 °C. From 328 to 473 h a nearly complete recovery occurs under illumination (Fig. 3), during the same time interval the cells stored in the dark at room temperature show only a minor recovery (Fig. 4).

The degradation/recovery behavior is dependent on the applied electrolyte. In contrast to cells with electrolytes based on acetonitrile or other organic solvents, cells based on ionic liquids as a solvent hardly degrade at 85 °C in the dark, though the cell efficiency of this system in sealed devices is substantially lower due to charge transport limitation [15,16]. In sealed cells efficiencies of approximately 1–2% can be reached using ionic liquids like HMI. In open cells the distance between the electrodes is minimized, resulting in approximately 5% efficiency. This result is a good proof of principle for the temperature stability of a nc-DSC.

The degradation pattern of the solvent-based electrolytes is dependent on the exact electrolyte composition. As can be seen in Figs. 3 and 4, the three cells filled with electrolytes EL 1 and 2 have a much stronger response to the cycling between annealing and illumination than the cell with

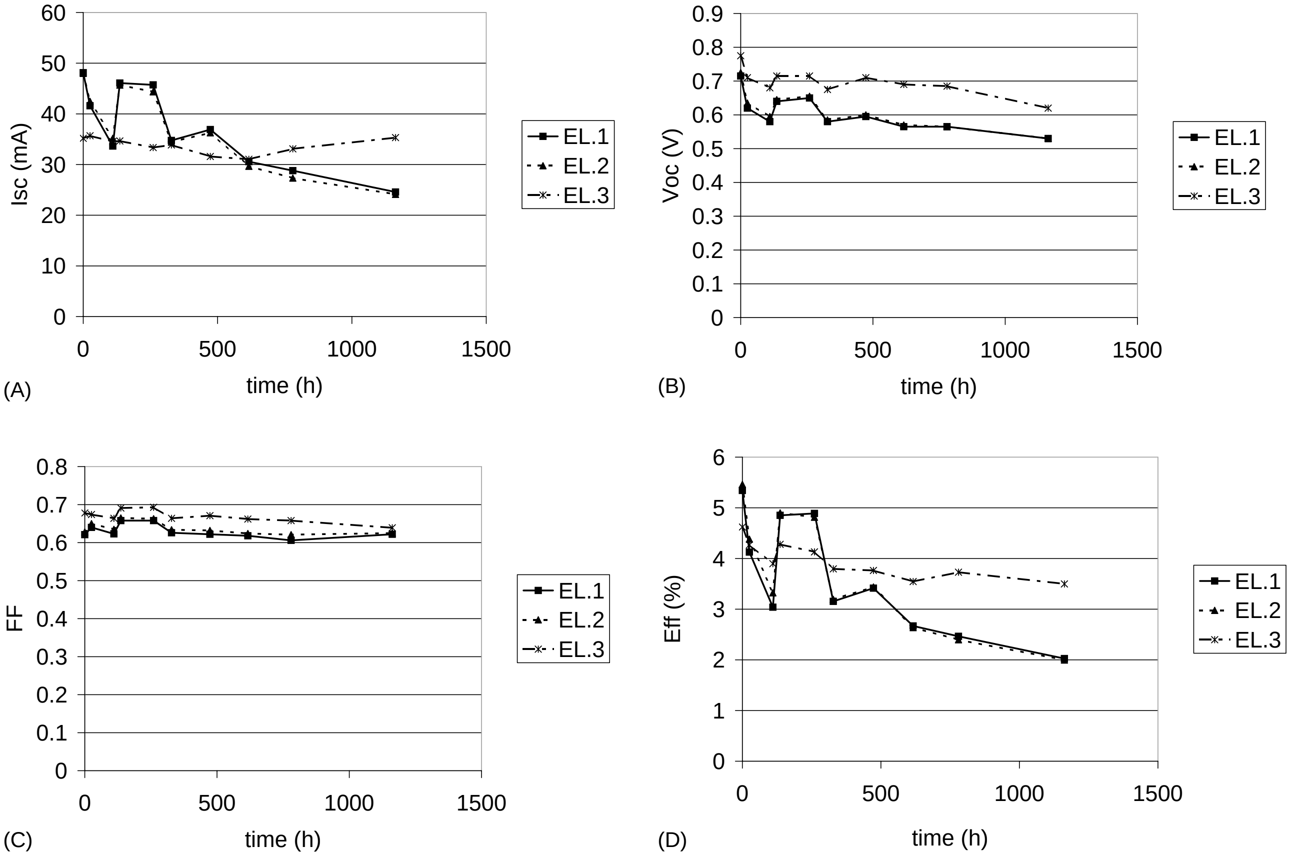

Fig. 4. Stability data for three cells depending on conditions—from 0 to 110, 260 to 328 and 473 to 1162 h: 85 °C, dark; from 110 to 260 h: 45 °C, 1 sun; from 328 to 473 h: 20 °C, dark: (A) I_{sc}; (B) V_{oc}; (C) FF; (D) Eff.

electrolyte EL 3. The electrolyte that results in a more stable behavior contains an increased concentration of iodine (0.1 M instead of 0.05 M) and does not contain TBP and LiI, NMBI has been used instead of TBP. At this moment it is not clear if and how this plays a role in the cell degradation at elevated temperatures. The iodine concentration has been chosen as one of the variable electrolyte parameters to check whether iodine depletion could be prevented by higher $[I_2]$. In this case no iodine depletion could be observed in both the 0.05 and 0.1 M electrolytes.

The adsorbed dye on the TiO_2 surface is in equilibrium with dye dissolved in the electrolyte. One could understand a shift in this equilibrium depending on the temperature, i.e. dye desorption could be the cause of lower performance for cells stored at elevated temperatures, with dye readsorption as a recovery process. In the case of ionic liquids as a solvent this equilibrium could be different from the case for organic solvents, explaining why the ionic liquids result in a better stability. However, this cannot explain why illumination dramatically enhances the recovery process. The dye adsorption/desorption equilibrium is also influenced by other surface-active components present. TBP being such a compound could lead to enhanced desorption of dye, thus explaining the difference in TBP and non-TBP containing electrolytes. Ambient contaminants like water can also influence the dye desorption making the results dependent on the exact processing conditions. These explanations for the observed phenomena, however, remain speculative.

As illumination is shown to be beneficial to cells that have been degraded at elevated temperatures, it is interesting to investigate if illumination in combination with the elevated temperatures is able to slow down or prevent the process of degradation. Another very good reason for carrying out such an experiment is the fact that an elevated temperature in the dark is a non-realistic testing condition (though it is still a valuable test) for a solar cell, it will never occur during outdoor application of the solar cell modules. Under outdoor conditions high temperatures are combined with high intensity levels of illumination. Depending on the climate, the light absorption and construction of the solar cell module, temperatures around 80–85 °C can be reached under outdoor conditions.

Realistic testing conditions also apply to the electrical conditions of each cell, i.e. in the optimal system cells should operate in the maximum power point. This can be realized by application of appropriate resistors.

3.3. Thermal annealing/illumination combined

Approximately 1 sun constant illumination was combined with a “worst case” constant heating of the device to 85 °C for cells under electrical load, in maximum power point

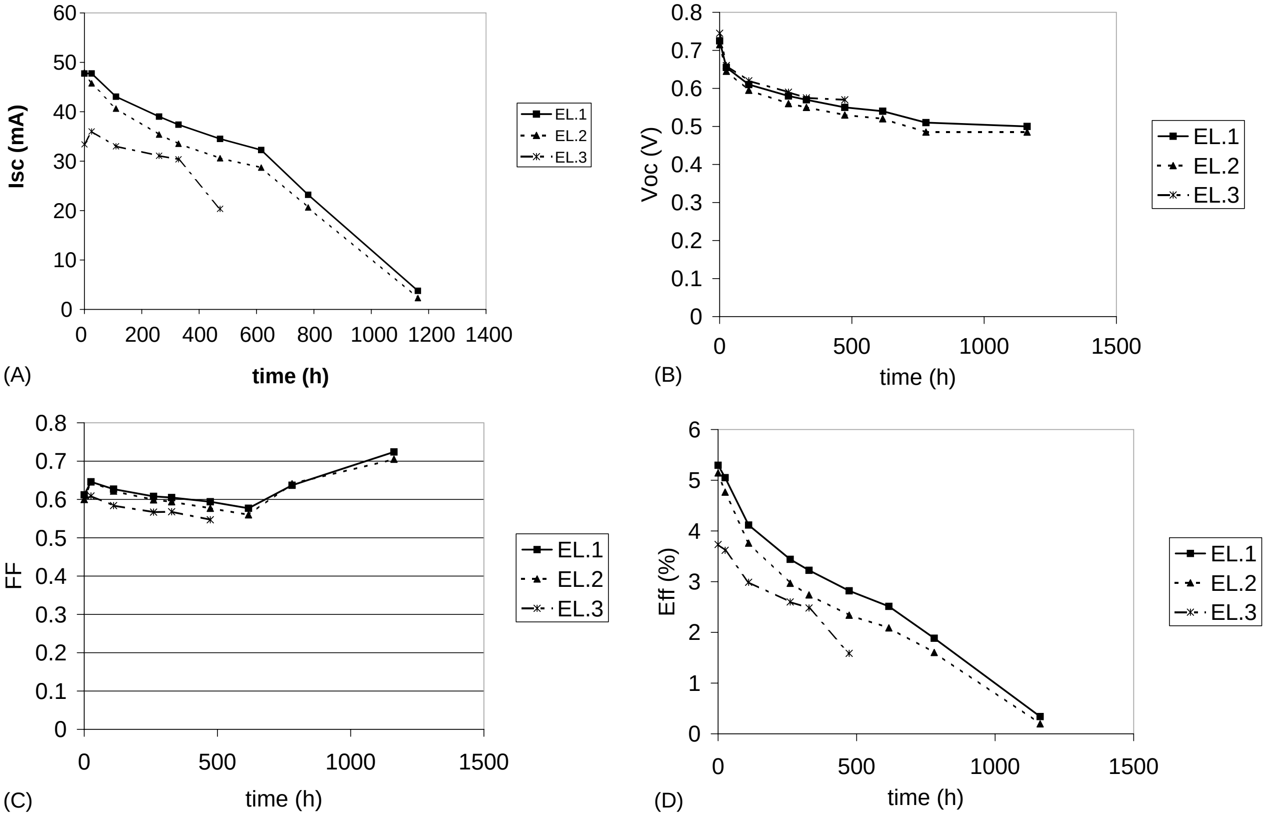

Fig. 5. Stability data for three cells under constant illumination of 1 sun at 85 °C. Note: the cell filled with EL 3 started leaking at approximately 500 h: (A) I_{sc}; (B) V_{oc}; (C) FF; (D) Eff.

(Fig. 5). This resulted in a more severe decrease in cell performance than at 85 °C in the dark, in contrast to what could be expected based on the results from the 85 °C/illumination cycling test described in Section 3.2.

When the degradation in the interval from 473 to 1162 h in Fig. 5 is compared to the degradation in Fig. 4, for the same interval, it shows that under illumination of approximately 1 sun at 85 °C the degradation is faster than in the dark/85 °C situation. In the dark the degradation tends to slow down from 600 to 1200 h, however, under illumination the performance keeps going down at a relatively constant rate, ending at much lower efficiency values after 1200 h of testing. Compare the interval from 616 to 1162 h for master plates stored at 85 °C/dark (Fig. 3) and those stored at 85 °C/1 sun (Fig. 5). In this interval the cell filled with EL 1 degrades from 2.60 to 1.82% at 85 °C/dark (Fig. 3). The degradation for the same type of cell is much more severe at 85 °C/1 sun from 2.51 to 0.34%. The electrolytes of all cells under illumination at 85 °C bleached severely by loss of iodine in contrast to the electrolytes of the cells that were kept in the dark at 85 °C.

4. Conclusion

Dye-sensitized solar cells based on different electrolyte compositions have been subjected to aging tests. A thermal stress test under both illuminated and dark conditions has been carried out, as well as a light-soaking test. Constant illumination under 1 sun (artificial) at room temperature does not impose a large stress onto the solar cell. Constant heating in the dark at 85 °C leads to a severe decrease in performance which is somehow reversible, i.e. the efficiency of degraded cells can be restored by continuous illumination of approximately 1 sun at moderate temperatures. A reference restoration experiment in the dark at room temperature revealed that illumination is essential to enhance this restoration process. The sensitivity of the cells towards degradation at elevated temperatures is dependent on the electrolyte composition. Cells based on electrolytes with a higher I_2 content and without TBP and LiI tend to be less sensitive towards high temperatures, though initial efficiencies are lower. For all electrolyte compositions the test at 85 °C under constant illumination appeared to result in the most severe decrease in cell performance. It should be noted that these conditions are non-realistic with respect to a day/night cycle, the illumination at 85 °C has been applied constantly, i.e. no potential recovery in the dark has been allowed.

It is important to realize that apart from cell composition also the purity of the starting materials and the processing conditions play an important role in the stability of the manufactured solar cells. For instance humidity can have a serious impact on cell performance and stability. For this reason, the results presented in this paper are not valid in general but should be considered as specific for the laboratory in which the processing has been carried out.

The IEC test has been developed as a qualification test for thin film and crystalline silicon modules. As such it is not valid to make extrapolations for outdoor lifetime. It is rather meant as a tool to qualify the mechanical integrity of the complete module in relation to thermal stress and humidity. The test does not fit to the nc-DSC since the issues of intrinsic chemical stability (both thermal and UV, typically for the nc-DSC) are not addressed. This study reveals that for nc-DSCs it is important to test under conditions close to natural outdoor conditions. The IEC test can be too pessimistic: at 85 °C in the dark degradation occurs, according to IEC testing the nc-DSC does not pass this test. However, it is proven that this effect can be compensated by illumination, resulting in a recovery of the cell performance.

On the other hand, the IEC test can be too optimistic, degradation for nc-DSCs is more severe at 85 °C in combination with illumination than at 85 °C in the dark, according to IEC procedures. In other words, if nc-DSCs would pass the test for annealing at 85 °C in the dark this does not imply a stable power output for nc-DSCs at elevated temperatures under outdoor operating conditions.

5. Future outlook

A relevant test should be developed for nc-DSCs mimicking natural outdoor conditions, addressing the issues previously mentioned. Apart from this, cells should be tested under different real outdoor conditions and also under more demanding outdoor conditions, i.e. high temperatures under illumination, like in a desert climate.

Commercialization is strongly dependent on developments in the field of stability. Though very promising results have been achieved by application of the hydrophobic dye, the understanding of the mechanisms of cell degradation is insufficient. In production it could be mandatory to apply defined conditions considering the purity of chemical ingredients and the composition of the ambient air, i.e. a dry room could be applied for processing steps in which the air humidity is critical. For research in the field of nc-DSCs this could also help to generate results that are independent of the laboratory in which the cells have been processed.

Acknowledgements

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