LONG-TERM STABILITY AND EFFICIENCY OF DYE-SENSITIZED SOLAR CELLS

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ABSTRACT: For the first time, a certified AM1.5 efficiency of 8.2% has been reached for nano-crystalline dye-sensitized solar cells (nc-DSC) on areas larger 1 cm^2; i.e. 2.5 cm^2. It has been further proven, that 2-valent salts like MgI_2 and CaI_2 as additives to the electrolyte have a strong stabilising effect during UV-illumination. Tests under continuos light soaking for several thousand hours demonstrate the ability of nc-DSCs to operate for at least 5 – 10 years under outdoor illumination conditions without major degradations. Continuos and periodic thermal tests according to IEC 1215 norms are promising but with 30% to 40% loss in efficiency still critical.

Keywords: Solar Cell-1: Dye sensitisation-2: Stability-3: Efficiency-4:

1. INTRODUCTION

For a successful introduction of nano-crystalline dye sensitised solar cells (nc-DSC) [1] for outdoor applications, specifically for large area power applications, several factors are of importance: technical performance and manufacturability, costs, design, market demand and long term stability. During last years, the long-term stability of nc-DSCs has been investigated extensively in the frame of the European project LOTS-DSC [2]. For this purpose, a large number of nc-DSCs has been manufactured on so-called masterplates: five individual cells of 4 cm^2 each on 7.5 x 10 cm^2 plates. The aim has been a high reproducibility in order to investigate the small deviations that occur upon degradation. In addition, nc-DSCs with improved cell design but same materials have been manufactured in a similar manner (2.5 cm^2 active area per cells) with the aim to reach optimum efficiencies. At various test sites, cells have been exposed continuously for months to ultraviolet light, 1-sun equivalent light soaking and thermal stress conditions. Also, outdoor testing and temperature cycling has been carried out.

2. EXPERIMENTAL

2.1 Measuring objects; masterplates

The nc-DSCs are fabricated on a common SnO_2:F-glass substrate (LOF-TEC8, 3 mm, 8 Ohm/square). TiO_2 layers are deposited by screen printing. The synthesis of the nc-TiO_2 particles and the formulation of a screen print paste have been similar to the ones described earlier [3]. A screen printed silver strip on each side of each cell ensures proper current collection within the masterplate. Also, SnO_2:F-glass substrates coated by screen printing with a thin pyrolithic platinum layer are used as the counter electrodes. Both electrodes are fired usually at 450 - 500 ^oC for 30 minutes. Surlyn 1702 (DuPont) hotmelt foil has been used as the primary sealing material for cells aged below a temperature of 60 ^oC. The distance between the electrodes is approximately 25 μm in this case. A representative picture of a masterplate during fabrication is shown in figure 1. The sensitising dye used for the masterplates was cis-di(thiocyanato)-N,N' bis(2,2"bipyridyl4,4'-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 ^oC for 30 - 60 minutes.

Cells, which undergo stability tests above 60 ^oC cannot be sealed with Surlyn 1702. Hotmelts with higher melting points or hermetic sealing materials are required then. In particular, a different sealing technique has been developed which makes use of a low temperature melting glass frit. The composition of the glass frit has carefully been adjusted in order to match the thermal expansion coefficient of the glass plates. The actual sealing (fusing) of the master plates takes place at a temperature of 650 ^oC for several minutes. No mechanical pressure is applied during the fusing step. Also, a modified coloration solution is applied in this case consisting of a higher concentrated solution (5 mM) of dye N719 in a 3:1 acetonitrile and tert-butyl pyridine mixture. After application of the electrolyte, the filling holes are carefully sealed with the help of a hotmelt foil made from Bynel (DuPont) and a thin glass cover. The results indicate that for all measured photovoltaic parameters the reproducibility for 5 cells on one masterplate can be achieved with an accuracy of +/- 7.5%. In the case of glass frit sealed master plates similar performance is achieved. In some cases, a white light scattering porous layer made from ZrO_2 [3,4] has been screen printed on-top of the TiO_2 layer.

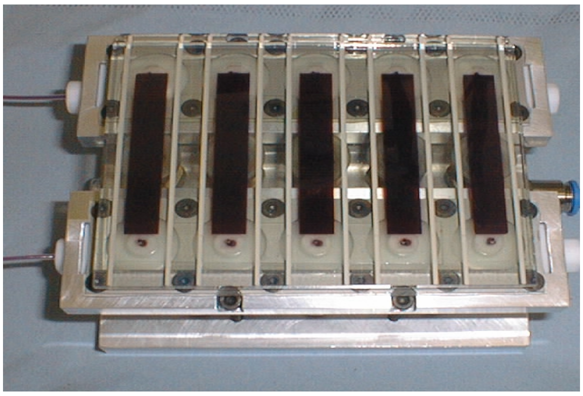


Figure 1: Processing of a master plate (75 mm x 100 mm) containing 5 individual dye sensitised test cells (active area 4 cm^2). The coloration step, flushing of dye solution after sealing through holes on a filling unit, is shown.

2.2 Characterisation and ageing

Continuous strong light soaking and on-line characterisation of the photovoltaic parameters is done in identical sites. 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.

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 TiO_2 in the cell. The UV-intensity is 10 mW/cm^2 at the sample area. The cell temperature is kept constant at 20 ^{o}C.

Outdoor measurements have been performed at ECN in the Netherlands and INAP in Germany. The master plates have been protected by a window glass against rain.

Periodic thermal ageing has been performed in standard climate chambers according to IEC norms.

3. RESULTS

3.1 Efficiency

Cell	I_{sc} mAcm^{-2}	V_{oc}	FF (%)	η(%)
Background Copper plate				
1835	14.9	0.733	71.2	7.78
1836	15.0	0.728	71.2	7.80
1838	15.3	0.728	69.9	7.80
1839	15.6	0.727	71.3	8.10
White background				
1838	15.4	0.726	71.0	7.97
1839	15.8	0.725	71.6	8.18

Table 1: Best efficiency values reached so far for cells on masterplates (active cell areas 2.5 cm^2). Measurements are carried out at FhG-ISE and certified for AM1.5 conditions.

Certified efficiencies of up to 8.2% have been reached for cells on master plates (table 1). In this case the active cell width has been 8 mm, the active cell area being 2.5 cm^2. The current has been collected on both sides of the electrodes. The electolyte used for these plates was 0.6 M HMII, 0.1 M LiI, 0.05 M I_2, 0.5 M TBP in acetonitrile. It should been noted, that the efficiencies have been measured 2 months after preparation and storage at room temperature.

3.2 Accelerated ageing

The influence of additives like MgI_2, CaI_2 and 2-phenylimidazole in various electrolyte compositions have been studied and more recent results are shown in figure 2. It can be seen that both MgI_2 and CaI_2 show strong UV-stabilising effects.

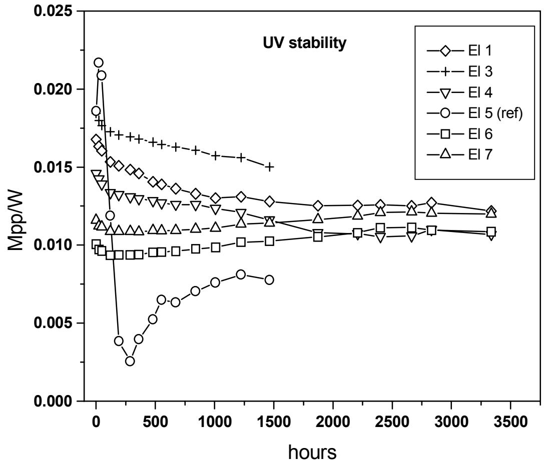


Figure 2: Stability data (maximum power point) of cells on masterplates after ageing with a UV-light tester (cell temperature 35 ^{o}C). Electrolyte no. 5 is the (unstable) reference without additive

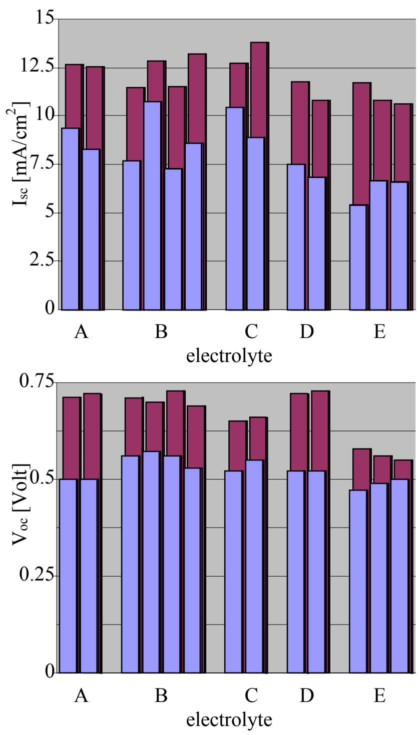
El 1	0.5 M MgI_2, 0.3 M HMII, 0.6 M TBP, 30 mM I_2
El 3	0.2 M CaI_2aq, 0.4 M HMII, 40 mM I_2, 1.3 M TBP
El 4	0.6 M CaI_2aq, 0.3 M HMII, 40 mM I_2, 1.3 M TBP
El 5	0.5 M HMII, 40 mM I_2, 0.7 M TBP
El 6	0.2 M. CaI_2aq, 50 mM I_2, 0.42 M 2-phenylimidazole
El 7	0.2 M. CaI_2aq, 0.5 M HMII, 50 mM I_2, 0.42 M 2-phenylimidazole

Table 2: Electrolyte compositions in the notations of figure 2. HMII (hexylmethylimidazolium iodide), TBP (4-tert-butyl pyridine), solvent in all cases acetonitrile. MgI_2 and CaI_2 are dissolved at 60 ^{o}C in a HMII/acetonitrile mixture prior to further dilution.

More than 100 Surlyn (duPont) sealed masterplates were exposed continuously to visible light from 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 stability results that were obtained from these tests show some striking differences in stability when various electrolyte solvents are used. For instance, cells containing methoxyacetonitrile show poor stability behaviour under these conditions, and a strong decoloration of the electrolyte indicating iodine loss is observed.

Propionitrile turned out to be a good choice of solvent and was mainly used in further stability tests. In the best cases a drop of only 15% in inital cell efficiencies (4-5%) after 4000 hours of illumination has been reached.

A large effort has been made to stabilise the cells at temperatures of 60 °C and above. The best result from thermal stress tests at 60 °C achieved thus far have been obtained for 5% efficient cells containing purified propionitrile as the electrolyte solvent. Nearly no decrease in cell efficiency after 2000 hours thermal ageing at 60 °C is observed. Various cells containing different electrolytes have been tested at 85 °C thermal ageing for 875 hours in order to study the influence of electrolyte additives. As solvents acetonitrile and propionitrile have been used. Some results and the electrolyte compositions are shown in figure 3. The initial cell efficiencies have been 4.5%. In the best case (electrolyte B) a decrease of only 30% has been observed. Measurements by electrical impedance spectroscopy (EIS) show, that after ageing the lifetime of the electrons in the TiO_2 is reduced from 20 ms to 10 ms.



Electrolyte compositions:

Electrolyte	A	B	C	D	E
Solvent	ACN	PN	PN	PN	PN
HMII [M]	0.58	1.50	2.04	0.66	0.66
LiI [M]	0.11	-	0.07	-	-
MgI_2 [M]	-	0.12	-	-	-
CaI_2 [M]	-	-	-	0.08	0.08
I_2 [M]	0.05	0.02	0.03	0.03	0.03
TBP [M]	0.52	0.57	-	0.80	-

Figure 3: Results from a thermal ageing test performed on various cells on master plates containing different electrolytes. The short circuit currents and open circuit voltages before and after ageing at 85 °C for 875 hours are displayed. Only cells that passed the visual inspection test (no major leakage of electrolyte) after ageing are shown. Notation of chemicals used: ACN - acetonitrile, PN - propionitrile, HMII - hexyl-methylimidazolium iodide, TBP - tert-butyl-pyridine.

Several master plates have been exposed to outdoor conditions over 1 year. Main failures have only occurred due to leakage at the filling holes. Best results are shown in figure 4.

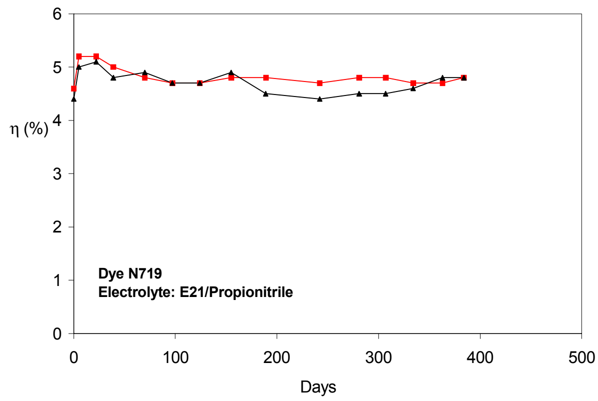


Figure 4: Best results from outdoor measurements of cells on master plates. Test location at Gelsenkirchen, Germany

Preliminary thermal cycling tests have been performed according to IEC (-40 °C to 85 °C, 200 cycles, duration 1 cycle 6 hours) on master plates which have been sealed by glass frit. Best results are shown in figure 5. The electrolyte solvent has been acetonitrile in this case. After 200 cycles a drop of approx. 40% in maximum power has been observed which to 20% is caused by a loss in fill factor, probably due to degradations problem at the electrical contacts.

Number Cycles	I_{sc} [mA/cm^2]	V_{oc} [V]	FF	MPP [mW/cm^2]
0	17,6	0,730	0,482	6,23
145	14,1	0,645	0,402	3,60
200	13,7	0,65	0,401	3,58

Figure 5: Best results from preliminary thermal cycling (IEC 1215, IEC 518/93). Cells are measured under 0.7 suns, values are corrected for 1 sun illumination.

Several glass sealed master plates have been prepared with electrolytes which contain artificially added impurities. In table 3 the initial performance of the cells are shown. There is some trend that iodinated species (iodoethane, iodoacetic acid) in concentrations above 0.2 M lower the photovoltage. This could be a consuming reaction with TBP. Electron lifetimes were measured by means of EIS. The additives did not significantly affect these lifetimes, which were all in the range of 10-20 ms. Results after thermal ageing of the cells are still pending.

Additive	I_{sc} [mA/cm^2]	U_{oc} [V]	τ [ms]	conc.
none	16.98	0.700	13.2	-
	17.36	0.710	11.4	-
iodoethane	18.57	0.695	14.3	0.2 M
	17.92	0.655	17.7	0.6 M
H_2PtCl_6	19.20	0.710	15.5	5 nm Pt
	17.20	0.735	19.2	15 nm Pt
Iodoacetic acid	12.52	0.585	13.6	0.2 M
	11.60	0.585	18.0	0.6 M
Iodoacetonitrile	17.16	0.585	12.6	0.6 M
	17.19	0.580	11.8	0.6 M
TBASCN	18.41	0.720	16.1	0.18 M
Zinkiodid	19.73	0.695	-	0.1 M
	13.70	0.465	-	0.32 M

Table 3: Initial performance and electron lifetimes of glass sealed cells containing artificial impurities. Cells are measured under 0.7 suns, values are corrected for 1 sun illumination.

4. DISCUSSION AND CONCLUSIONS

For the first time, a certified AM1.5 efficiency of 8.2% has been reached for nc-DSC on areas larger 1 cm^2; i.e. 2.5 cm^2.

It has been further proven, that 2-valent salts like MgI_2 and CaI_2 as additives to the electrolyte have a strong stabilising effect during UV-illumination.

Tests under continuos light soaking for several thousand hours demonstrate the ability of nc-DSCs to operate for at least 5 – 10 years under outdoor illumination conditions without major degradations.

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5. REFERENCES

[1] Grätzel M., Progress in Photovoltaics: Research and Applications 2000; **8**: 171-18

[2] A. Hinsch, J.M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer, J. Ferber, Progress in Photovoltaics: Research and Applications 2001, in press

[3] Burnside S., Winkel S., Brooks K., Shklover V., Grätzel M., Hinsch A., Kinderman R., Bradbury C., Hagfeldt A., Pettersson H., Journal of Material Science: Materials in Electronics 2000, **11**: 355-362

[4] A. Hinsch, R. Kinderman, M. Späth, E. Rijnberg, J.A.M. van Roosmalen, Proceedings 2nd World Conference and Exhibition on PV Energy Conversion, Vienna 1998.

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