Long term stability of dye-sensitised solar cells for large area power applications

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To be able to commercialize the dye-sensitised solar cell (DSC) technology for large area power applications it needs to be clear what module life-times can be obtained. Therefore, the long term stability of DSCs is investigated. Accelerated tests are performed in order to determine the lifetime of DSCs. Stability results over 10000 h were obtained with small, individual cells. It is shown that the chemical composition of the cells is very important, even water can be tolerated to some extend. For more sophisticated investigations, DSCs for the stability tests are processed on so-called masterplates: five individual cells on one glass plate. Cells with an efficiency of 5% have been produced. The cell parameters (I_{sc}, V_{oc}, FF, η) varied only by less than 7.5%. Several masterplates with different components were produced and aged. Stability test stands were developed for long term stability testing, allowing 96 masterplates (480 cells) to be aged in parallel. The masterplates are aged under continuous illumination and electrically characterised in-situ. First stability results were obtained with different solvents.

Keywords: dye-sensitised solar cell, photoelectrochemical cell, long-term stability.

1. Introduction

A dye-sensitised solar cell (DSC) consists of three main components: A dye-covered nanoporous TiO_2 layer (photoelectrode) on a glass substrate coated with a transparent conductive oxide (TCO), an iodide/triiodide redox electrolyte, and a platinized TCO-coated glass as counter electrode (Fig. 1). The pores of the TiO_2 layer and the gap between the electrodes are filled with the electrolyte [1,2]. A DSC is a photoelectrochemical cell. Degradation factors and mechanisms of DSC under long-term operation are different from those experienced in solid-state solar cells.

Up to now the long term stability of DSCs has not been studied sufficiently enough to allow an extrapolation of stability data to a 10-year outdoor operation equivalent. Stability data are presented from measurements of a large number of test cells that have been processed on masterplates. The work presented is part of an on-going test program. During the program, accelerated ageing will be done in order to determine the lifetime of a DSC. The cells are continuously (day and night) operated under "1 sun" equivalent illumination. A high number of test samples is produced with different cell components to identify the degradation effects and to get a better knowledge about the components which will lead to stable cells.

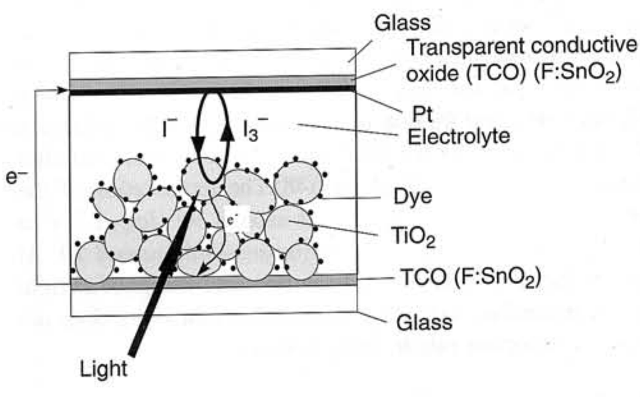

Fig. 1. Schematic structure of a dye-sensitized solar cell (DSC).

In this paper, the influence of different electrolytes and solvents on the long term behaviour of the short circuit current is investigated.

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2. Measurement objects

2.1. Single cells

Single cells were prepared according to methods described in literature [2,3]. They were not specifically high efficiency cells and had an area of approximately 2–2.5 cm^2.

2.2. Masterplates

Up to now one problem was the lack of reproducibility in cell construction, which prohibited a systematic investigation of the influence of cell composition on long term stability. Therefore, for more sophisticated and statistical investigations the DSCs for the stability tests were processed on so-called masterplates: five individual cells of 5×0.8 cm^2 on a glass substrate of 7.5×10 cm^2. This allowed a high reproducibility in order to investigate the small deviations that will occur upon degradation. Efficiencies of 5% have been obtained reproducibly. The deviations of the cell parameters (I_{sc}, V_{OC}, FF, η) within one masterplate were (±7.5%. A representative picture of a masterplate is shown in Fig. 2. In Table 1, data of the cells from 2 masterplates are given.

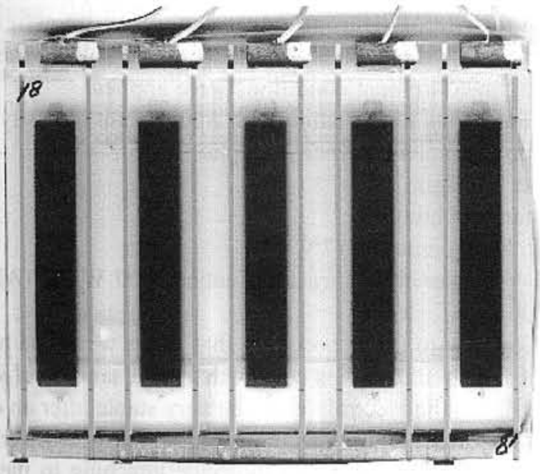

Fig. 2. Picture of a masterplate.

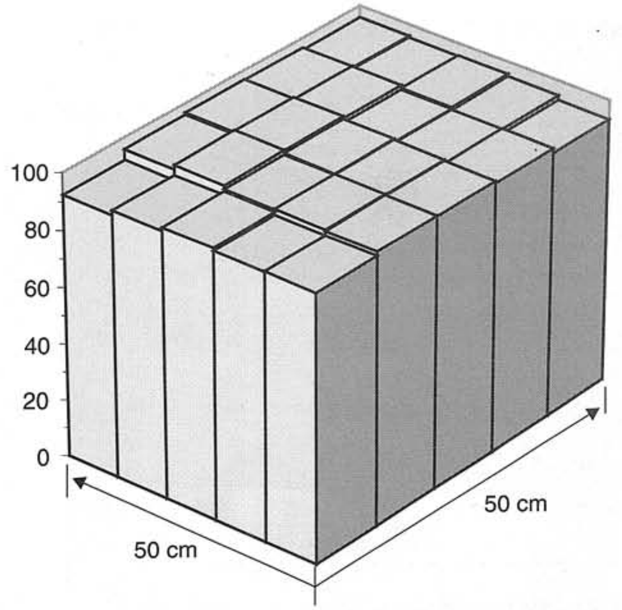

Fig. 3. Homogeneity of the sulphur lamp.

3. Stability test stands (sulphur lamp system, visible light)

Stability test stands (sulphur lamp systems) were developed for long term stability testing. A representative example of two sulphur lamp system units is shown in Fig. 4. One unit consists of automated measurement facilities for 80 cells (16 masterplates). 480 cells can be aged in parallel. The spectrum of the sulphur lamps is shown in Fig. 5. The intensity can be varied up to two sun equivalent intensity, but is operated at one sun equivalent intensity.

With the stability test stands accelerated ageing is done in order to determine the lifetime of DSC. The masterplates are continuously operated under one sun equivalent intensity. The stability test stands will run over at least two years. As the homogeneity (Fig. 3) and stability of the sulfur lamps is sufficient, the masterplates are aged

Table1. Data from cells of 2 masterplates, measured under an irradiance of 1000 W/m^2.

Masterplate and cell number	J_{sc} (mA/cm^2)	U_{oc} (V)	FF (%)	Efficiency (%)
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

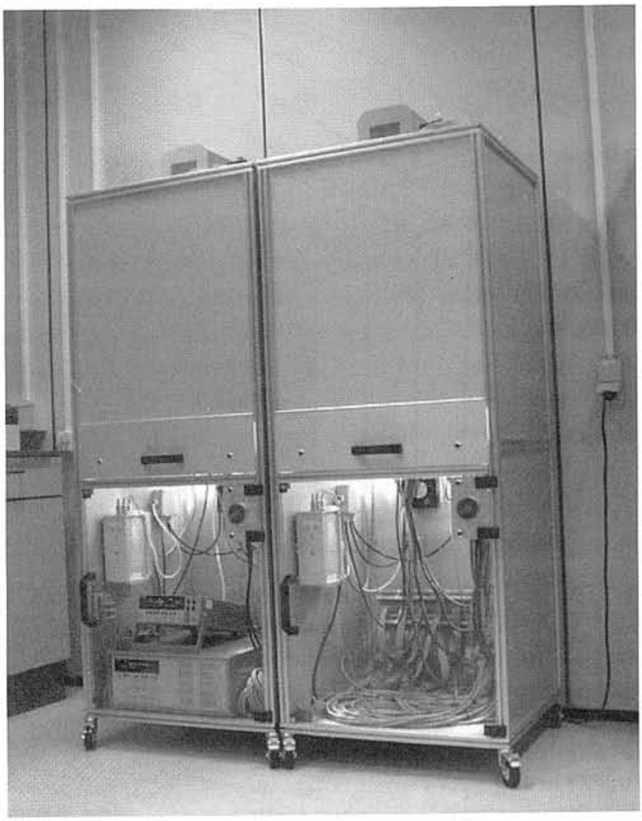

Fig. 4. Two sulphur lamp test stands.

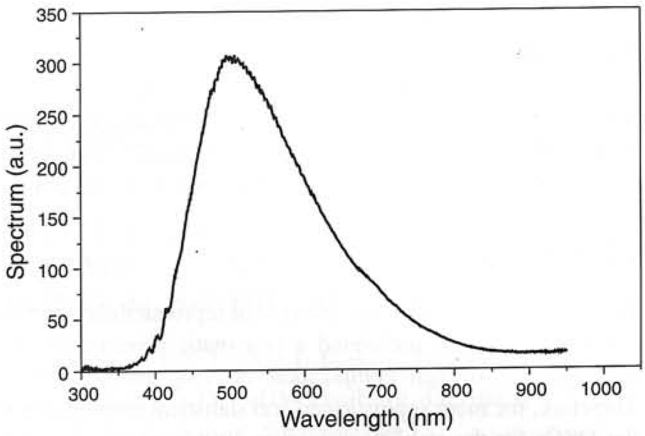

Fig. 5. Spectrum of sulphur lamp.

and electrically characterised in that stability test stands. In Fig. 6 a series of masterplates placed in a built stability test stand is shown.

In order to control the measurement conditions of the different stability test stands, the stability test stands are equiped with a permanent irradiance and temperature control unit. Beside this, 8 reference cells (crystalline silicon) were built and calibrated at Fraunhofer ISE, PV Calibration Laboratory, with a class A simulator. With this equipment it is possible to compare measurement results obtained at the different test stands.

4. Stability results

4.1. Stability results of single cells

Stability results (see Fig. 7) over 10000 h were obtained with small, individual cells. The cells had the following electrolyte compositions: 0.5 M LiI, 0.05 M I_2 in methoxypropionitrile. Different additives were investigated: 4-tert-butylpyridine (0.3 M) and water (5 vol%). The following measurement conditions were applied:

- continuous illumination with a high light intensity (2.5 sun equivalent intensity, sulphur lamp),
- no UV light,
- standard humidity,
- low temperature (17°C),
- I-V curves were measured under 1000 W/m2 (AM1.5 global).

Contrary to the expectation that water would be harmful, it appeared that even cells with a small amount of water (5 vol%) to the electrolyte can be very stable after an equilibrium period, as long as the additive 4-tert-butylpyridine (TBP) is present. TBP is a molecule attaching to the sur-

Fig. 6. A series of masterplates placed in a stability test stand.

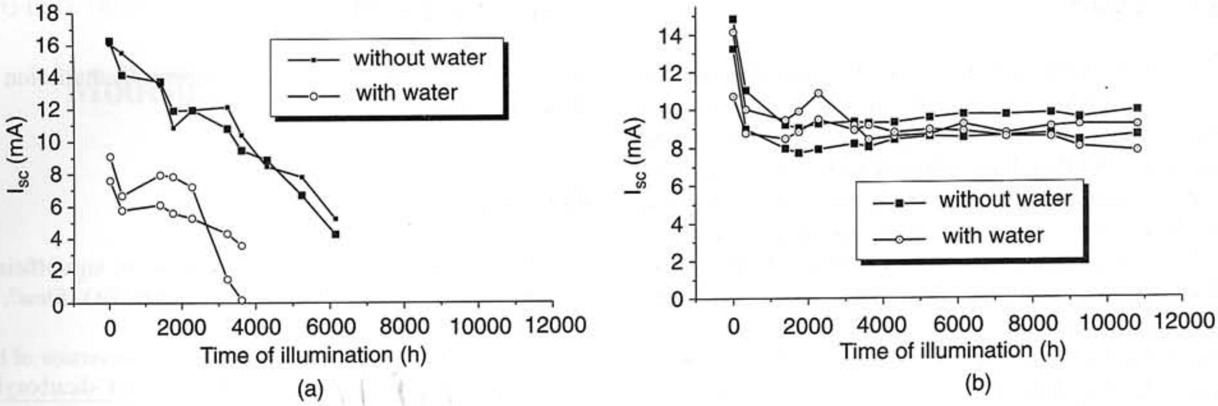

Fig. 7. Short-circuit current I_{sc} of single cells with different components. The cells were aged under a continuous 2.5 sun equivalent intensity and measured under 1000 W/m^2 (AM1.5gl): single cells without 4-tert-butylpyridine (a), single cells with 4-tert-butylpyridine (b).

face of TiO_2 and probably shields the TiO_2 surface which is not covered with dye. Thus unwanted side reactions are probably suppressed.

4.2. Stability results of masterplates

Stability results of masterplate cells with different solvents are shown in Fig. 8. The cells had the following electrolyte compositions: 0.6 M HMI, 0.1 M LiI, 0.05 M I_2, 0.5 M 4-tert-butylpyridine. The used solvents were acetonitrile, methoxyacetonitrile, propionitrile and methoxypropionitrile. The following measurement conditions were applied:

- continuous illumination in the sulphur lamp test stands (one sun equivalent intensity),
- no UV light,
- standard humidity,
- temperature 45°C,
- I–V curves were measured under one sun equivalent intensity in the sulphur lamp test stands.

In Fig. 8, the results of the first two months are shown. Cells with different solvents clearly show different behaviour in the long term stability. With this electrolyte composition propionitrile seems to be the most stable solvent.

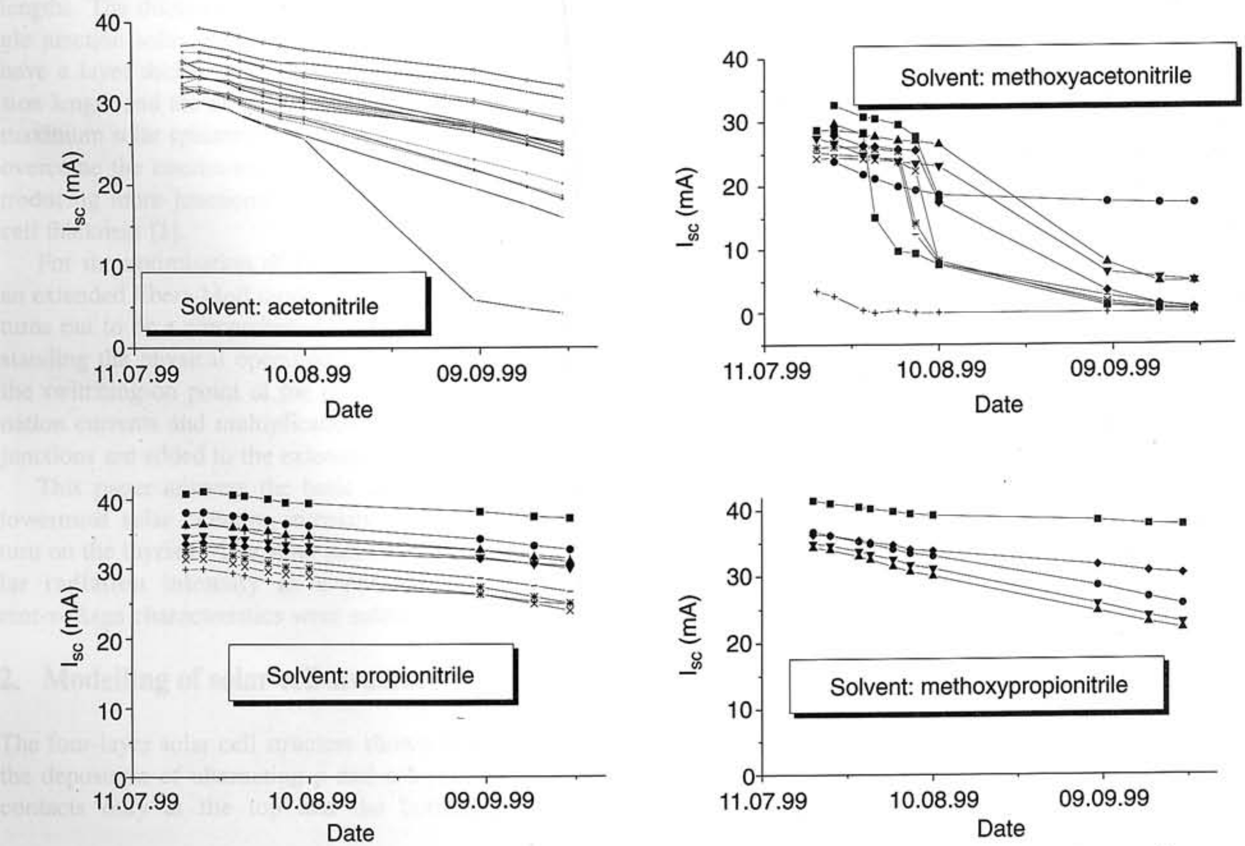

Fig. 8. Short-circuit current I_{sc} of cells on masterplates with different solvents. The cells are aged and measured under a continuous one sun equivalent intensity.

5. Conclusions

The long-term stability of DSC has been investigated. Accelerated tests under continuous illumination were performed in order to determine the lifetime of DSC. Stability results over 10000 h were obtained with small, individual cells. It is shown that the chemical composition of the cells is very important, even water can be tolerated to some extend. For more sophisticated investigations, DSCs for the stability tests were processed on so-called masterplates: five individual cells on one glass plate. Cells with an efficiency of 5% have been obtained reproducibly. The cell parameters (I_{sc}, V_{oc}, FF, η) within a masterplate varied only by ±7.5%. Stability test stands were developed for long term stability testing, allowing 96 masterplates (480 cells) to be aged in parallel. Stability results of masterplates showed a clear difference in stability behaviour with different electrolyte solvents. This shows the importance of this critical component on long term stability. The work presented is part of an on-going program on DSC device testing, accelerated ageing and interpretation.

Acknowledgements

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