

LONG TERM STABILITY OF DYE SENSITIZED SOLAR CELLS

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ABSTRACT: During accelerated lifetime testing of dye sensitized solar cells high temperature and intense illumination have been identified as critical stress factors. It is known that the choice of dye and electrolyte determines cell stability to a large extent. In this paper we have applied a combination of Z907 dye and a derivative of so called "Maxell electrolyte", which supports optimal cell stability. Several ageing tests have been carried out at elevated temperatures (up to 80°C) in the dark and under illumination conditions. TiCl₄ treatment of titanium dioxide is unexpectedly identified as an important factor to increase cell stability at high temperature. The nature of the nanoporous TiO₂ film is greatly changed by this treatment. Interactions between the modified TiO₂/dye/electrolyte also influence the sensitivity of the system towards moisture. It appears that the modification of TiO₂ by means of a TiCl₄ post treatment is essential to realize a stable cell.

Keywords: Dye-Sensitized, Durability

1 INTRODUCTION

Stability of dye sensitized solar cells (DSC) is improving to acceptable levels for commercial applications, as shown in a number of publications on this topic and by the growing interest of companies in the technology. To prove a sufficient outdoor lifetime it is required for a PV module to pass standardized accelerated ageing tests according to the IEC 61646 protocol. Enclosed in the prescribed testing sequence are several different climate chamber tests under a range of variable conditions (-40 to 85 °C/ very dry to 85 % RH). High temperature has been identified as a critical stress factor for DSC regarding the intrinsic stability. Apparently in the DSC system unwanted side reactions are accelerated at high temperatures, resulting in a decrease of cell performance.

Although a complete mechanistic understanding of these side reactions is still lacking, good progress has been made in rendering DSC devices temperature-stable when it comes to the right choice of chemical ingredients¹. The purpose of this work is to implement this in single cells with a surface area of > 1 cm² and make DSC ready for passing accelerated tests according to test protocols derived from the IEC 61646 standard.

The DSC working principle involves (electro)chemical processes and reactions that require fine-tuning to favor the essential cell processes and to suppress unwanted side reactions. This holds for both efficiency and stability optimization. As stability is a key requirement for successful implementation of DSC, the strengths and weaknesses need to be scrutinized in this respect. Some cell components, like electrolyte and dye, have been successfully adapted towards an improved stability. The choice to adapt this organic part of the cell seems a logical one, since these components are potentially most vulnerable to degradation. We show that apart from the organic materials the inorganic and supposedly inert TiO₂ plays a key role in optimizing cell stability.

2 EXPERIMENTAL

Several DSC were manufactured using the concept of master plates² (Figure 2). Cell compositions have been

varied with respect to electrolyte and TiO₂. Prior to testing the DSCs have been sealed with a polymer hot-melt (Bynel) with adequate durability at the elevated temperatures. Indoor accelerated tests were carried out at elevated temperatures (constant conditions at 60°C and 80°C in the dark and under illumination, cells at open circuit) on DSC with surface areas of 4 cm².

The electrolyte used was composed of 0.1 M iodine, 0.6 M dimethylpropylimidazoliumiodide (DMPI) and 0.5 M N-methylbenzimidazole (NMBI) in propionitrile (PN).

Water was added to the electrolyte of some cells (5 %). As a sensitizing dye Z907 was used.

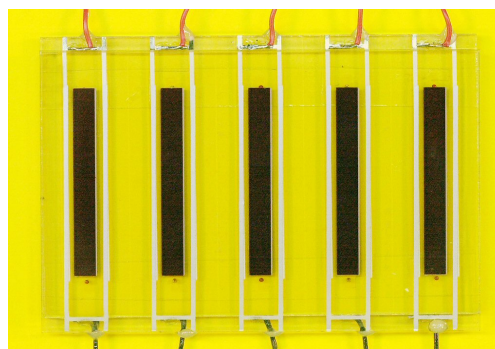


Figure 1: 5 individual cells on one "master plate"

3 RESULTS AND DISCUSSION

The best DSCs were able to pass an annealing test at 80°C during 1032 h, retaining more than 98 % of the initial performance (4.0 %), Figure 2. When the same test is carried out in combination with 1 sun equivalent illumination the decrease in performance is slightly accelerated, yielding 93 % of the initial performance after 1032 h at 80°C. A typical ageing pattern for DSC under these conditions is expressed by an initial rise in efficiency, followed by a slow decrease in the course of testing.

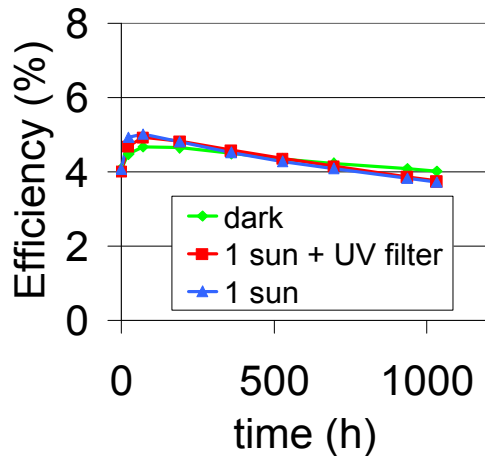


Figure 2: DSC efficiency with time at 80°C, under different conditions

The observed decrease in cell performance in the course of testing is mainly due to a decrease in open circuit voltage, J_{SC} and FF remaining relatively constant. It should be mentioned that the overall efficiency after 1032 h is based on a performance improvement of 15 % in the first 100 h followed by a decrease of 14 % in the remainder of the test period. The initial efficiency improvement relates to increased FF and J_{SC} .

At 60°C the conditions are more in favor of maintaining the initial performance improvement, resulting in a net increase of 13 % in the cell performance to 5,0 % cell efficiency after 1032 h at 60°C in the dark and a somewhat lower increase under illumination, Figure 3.

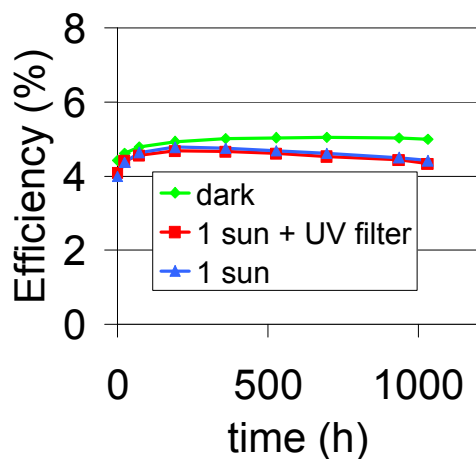


Figure 3: DSC efficiency with time at 60 °C under different conditions

Here the underlying improvement in FF and J_{SC} overcompensate the loss in V_{OC} with a net increase in efficiency as a result after 1032 h, as shown in Figure 4. Initially the IV curve reveals an anomalous shape at $t=0$, due to non-optimal functioning of the Pt catalyst. This results in a low fill factor. Upon ageing at elevated temperature the IV characteristics improve, although V_{OC} decreases.

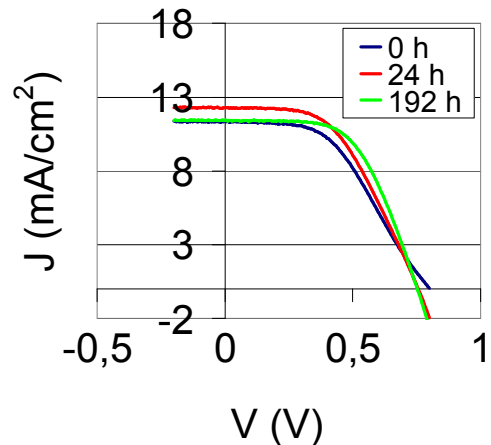


Figure 4: IV curves at different stages of ageing

The changes observed in the IV curves have been investigated in closer detail by means of electrical impedance spectroscopy. The resulting Bode plots are shown in Figure 5.

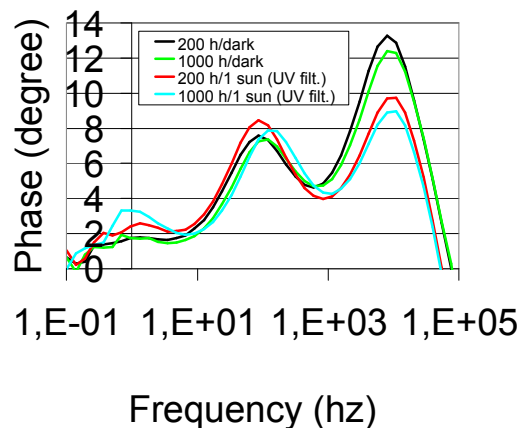


Figure 5: Impedance spectra (Bode plots) of aged DSC (at 80°C)

These plots of phase versus frequency typically reveal 3 peaks. From low to high frequency these peaks are related to respectively the ion diffusion in the electrolyte, the electron transport and recombination in the TiO_2 and the charge transfer at the counter electrode. A right shift in the peak values of the Bode plot is correlated with a decrease in resistance, in this case the resistance towards recombination of charge carriers from the TiO_2 and the charge transfer resistance of the Pt catalyst respectively.

The former results in a shorter electron lifetime in TiO_2 , which causes a lower V_{OC} and the latter results in improved charge transfer between Pt catalyst and electrolyte (conversion of I_3^- into I^-) enhancing FF.

As mentioned, DSC can be rendered temperature resistant provided that unwanted side reactions and degradation processes are effectively suppressed. This is obviously related to the organic materials used (dye and electrolyte composition) but apparently also to the inorganic TiO_2 part of the cell. Figure 6 illustrates a major influence of the condition of the TiO_2 on cell stability. In this case the nature of the TiO_2 film is changed by applying a post treatment with $TiCl_4$. This

treatment is used to create a thin layer of newly formed TiO_2 onto the existing particles comprising the nanoporous film.

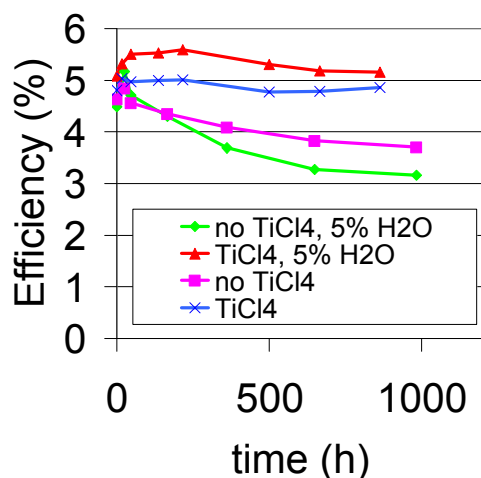


Figure 6: Effect of TiCl_4 post treatment on cell stability at $80^\circ\text{C}/\text{dark}$.

A known effect is the often observed improved cell efficiency, however our observations relate to a significantly enhanced cell stability for the TiCl_4 treated cells under accelerated testing conditions ($80^\circ\text{C}/\text{dark}$). The effect is even more pronounced in presence of moisture in the electrolyte (5% added water). A TiCl_4 post treatment renders the DSC much more resistant towards the adverse effects of water in the electrolyte.

4 CONCLUSIONS

Stability of dye-sensitized solar cells (DSC) is improving to acceptable levels for commercial applications. We have confirmed very encouraging stability results. The results obtained are in good agreement with data obtained in other labs for comparable cells with small surface areas ($< 1 \text{ cm}^2$)¹.

The surface properties of the titanium dioxide influence the DSC stability to a large extent as is revealed by the improved stability as a consequence of a TiCl_4 post treatment. By means of impedance spectroscopy a decrease in electron lifetime in TiO_2 upon ageing has been observed. This could be due to changes in the $\text{TiO}_2/\text{electrolyte}$ interface (i.e. formation of recombination pathways for electrons from TiO_2 to the electrolyte). A change correlated to increase of performance during ageing occurs at the counter electrode, which actually improves because of a decrease in charge transfer resistance. Ageing apparently results in removal of unwanted adsorbed species on the Pt catalyst.

OUTLOOK

The observations emphasize the necessity to study the dynamic behavior of DSC in more detail and develop adapted testing protocols to predict outdoor lifetime. Accelerated tests³ that run significantly beyond 1000 h are welcomed as they are complementary to existing tests and are required to make useful extrapolations to long exposure times. A survey of realistic potential outdoor exposure to high temperature would be helpful to put the

accelerated test data into perspective and establish an extrapolated outdoor lifetime.

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