Investigation of the long-term stability of dye-sensitized solar cells by optical and electrochemical impedance spectroscopy

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The long-term stability of electrochemical nanocrystalline dye-sensitized TiO₂ solar cells (DSC) is investigated. It may be distinguished between intrinsic (chemical) and extrinsic (due to non-adequate sealing) cell stability. The work presented focuses on the intrinsic stability of the DSC. Ageing of DSC under different stress factors is investigated: continuous visible light soaking, continuous UV-light soaking and temperature load [1], [2], [3]. In order to detect possible changes of inner electrical cell parameters during ageing, electrochemical and optical impedance spectroscopy measurements, as Electrochemical Impedance Spectroscopy (EIS), Intensity Modulated Photocurrent Spectroscopy (IMPS) and Intensity Modulated Photovoltage Spectroscopy (IMVS) were applied. Models for the DSC were developed, which are suitable for the evaluation of the impedance spectra. From both EIS and IMVS spectra the life time of the electrons \( \tau \) in the TiO₂ could be evaluated. It could be shown that the life time of the electrons in the TiO₂ depends strongly on the electrolyte composition. The life time decreases during ageing. As an example of the behaviour of an unstable cell three IMVS spectra of a DSC aged at 50°C in the dark are shown in Figure 1. The minimum in the imaginary part of the IMVS spectra shifts to higher frequencies during the ageing procedure. In Figure 2, the corresponding life time of the electrons in the TiO₂ is shown.

**Figure 1:** Unstable DSC aged at 50°C in the dark. IMVS measurements carried out before the ageing (0 days (---)), and after ageing (15 days (--), 27 days (-----)) at 50°C. The minimum in the imaginary part of the IMVS spectra shifts to higher frequencies.

**Figure 2:** Electron life time in TiO₂ evaluated from the IMVS spectra of Figure 1.
From EIS spectra of cells operated in the open-circuit mode under 1 sun bias intensity, additional information concerning properties of the electrolyte and the Pt-electrode can be obtained.

Accelerated ageing tests on a large number of nanocrystalline dye-sensitized solar cells showed, that in a first-order approximation a separation between the effects of visible light soaking, UV-illumination and thermal load on the long-term stability can be made. It was found that visible light soaking alone is not a dominant stress factor. A dramatic improvement of up to 3500 h in UV stability has been reached by adding MgI$_2$ to the redox electrolyte. Thermal stress pointed out to be one of the most critical factors determining the long-term stability of DSC: The life-time of a DSC under thermal stress is strongly related to the chemical composition of electrolyte solvents and additives. For cells containing pure nitrile-based solvents, electrolyte components and additives were found which result in encouraging stability results: 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 equivalent) good stability with 15 % decrease in efficiency could be demonstrated.

Up to now, Surlyn 1702 (DuPont) hotmelt foil was used as the primary sealing material. For the standard acceleration ageing test procedure for solar cells a temperature test at 85°C is needed. So far, it has not been possible to operate DSC at higher temperatures as 60°C due to the low melting point of Surlyn. Recently, a new sealing method was developed. DSC are now sealed with glasfrit. DSC sealed with glasfrit show a decrease of the short circuit current and open circuit voltage of about 17% after 875h at 85°C storage in the dark (Figure 3). The results are from an ongoing ageing test.

**Figure 3:** Decrease of the short circuit current and open circuit voltage. Cells aged at 60°C and 85°C in the dark. Cell aged at 60°C: Surlyn sealed cell. Cell aged at 85°C: Glasfrit sealed cell.

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