THE LUMINESCENT CONCENTRATOR: STABILITY ISSUES

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ABSTRACT: One of the major challenges in the research on luminescent concentrators is the lifetime of the luminescent polymer plates. There are some commercial plates available, but data on lifetime are very limited, especially when dedicated to applications like the luminescent concentrator. In this paper we report stability experiments on luminescent concentrator plates, aged under continuous white light illumination, outdoor conditions and high intensity monochromatic illumination. The results show that the lifetime strongly depends on the organic luminescent dye in the plate. The best materials exhibit an initial decrease in performance of about 20% and then remain more or less stable. It is shown that the degradation is not caused by UV illumination.

Keywords: stability, luminescent concentrator

1 INTRODUCTION

An interesting approach for conversion of light to electricity is the luminescent concentrator (LC). [1,2,3] The device allows concentration of light entering through a large front surface onto a small photo active area. A fundamental difference of the luminescent concentrator compared to other concentrator approaches is that it concentrates diffuse light as well as direct light. Tracking of the sun is not necessary. The motivation for pursuing the luminescent solar concentrator as with any concentrators is that if the receiver can be made much cheaper than solar cells, the LSC might offer a cost benefit.

The LC consists of a transparent matrix material, usually a flat plate, with solar cells connected to one or more sides. The transparent matrix contains luminescent particles such as organic dyes or quantum dots that absorb part of the incident solar spectrum. Part of the light emitted by the luminescent particles is guided towards the solar cells by total internal reflection. The LC has an important advantage over geometric concentrators as both direct and diffuse sunlight is collected, making solar tracking unnecessary, making them especially interesting for building integration applications.

Early studies on the LC resulted in a power conversion efficiency (η) of 4% for a stack of two LCs connected to GaAs cells[4]. The results were limited due to the low luminescence quantum efficiency of the available organic dyes and a large overlap between absorption and emission, causing re-absorption losses. Since then, organic dyes with improved stability and efficiency have become available. This, together with the availability of semiconductor quantum dots with a small overlap between absorption and emission, opens up the way to LCs with better efficiencies and stabilities. For this reason several groups are currently active in the development of LCs using improved luminescent dyes[5,6], rare-earth complexes[7], and semiconductor quantum dots[8,9].

Apart from the power conversion efficiency, a huge challenge for the LC is the stability. There are some manufacturers of fluorescent polymer sheets that give lifetime numbers. Cyro[10], for example sells fluorescent plates that have weatherability numbers of 3-5 years. The Italian company Madreperla mentions similar numbers in a private communication. These numbers are comparable with the best literature values mentioned in LSC applications.[11,12] The origin of the limited stability is degradation resulting from a combination of light and additives of the polymer matrix as well as remaining monomers in the matrix.[11,13,14].

In this paper we study the stability of LCs under continuous white light illumination, outdoor conditions and high intensity monochromatic illumination. Both the absorption as well as the external quantum efficiency of the LCs is studied as a function of illumination time.

2 EXPERIMENTAL

Our luminescent concentrator (LC) consists of a clear PMMA matrix doped with one ore more dyes. The LC plates that are used in this study are made at the Fraunhofer institute for Applied Polymer Research (FhG-IAP) and consist of a transparent polymer, Plexit55, of which the monomer is commercially available. The luminescent dye is added to the monomer solution and filled into moulds. Azoisobutyronitrile was used as the initiator in the polymerization at a concentration of 0.05%. Homogeneous, bubble-free plates were obtained after thermal polymerization. After the polymerisation, plates were removed from the mould and the sides were polished to obtain good, optically flat surfaces.

For the experiments described in this paper, the dyes Fluorescence Yellow CRS 040 (CRS040) from Radiant Colour and Lumogen F RED305 (RED305) from BASF were used. The 5 mm thick LC plates were doped with

CRS040, RED305, or a combination of these dyes and were divided in several 5x5 centimeter squares. RED305 was chosen for this experiment because of its relatively high stability and luminescence efficiency, which was confirmed in a preliminary ageing experiment. The drawback of RED305 is that it only absorbs a small part of the solar spectrum. For this reason a second dye was added that extends the absorption ramp and has an emission spectrum that overlaps with the absorption spectrum of RED305, thereby allowing radiative energy transfer. Furthermore, CRS040 has a high luminescence quantum efficiency.

The LC's where divided into three groups. The first group was aged outdoor, the second group was aged indoor by illumination with the solar test facility (STF) and the third group was kept in the dark as a reference. During the ageing the UV/VIS absorption spectra and external quantum efficiency (EQE) spectra of the LC's were measured at regular time intervals to record the stability of the dyes in the LC's and the overall performance of the LC's.

A separate series of LC's doped with RED305 and CRS040 were made for a high intensity, monochromatic light ageing experiment.

Absorption measurements were performed using a HP 8453 diode array UV-VIS spectrophotometer in the wavelength range 300-1100 nm.

EQE measurements were carried out using a home-built set-up, consisting of a 1000 W xenon lamp, 34 band pass interference filters and four 150 W halogen lamps for the bias illumination. Measurements with and without bias illumination gave similar results. The reported spectra in this paper are measured without bias illumination. For these measurements a standard mc-Si solar cell was attached to the LC plate using microscope immersion oil with a refractive index of 1.49. After the measurements, the mc-Si solar cell was removed, the LC's were cleaned and the ageing was continued.

Alongside the 'home made' LC's, several LC's from commercial fluorescent plate material were aged and measured to compare the performance of commercial material to the home made LC's.

Outdoor ageing

For the ageing outdoor the LC's were placed under a tilt angle of 30 degrees in our outdoor test facility (see Fig 1). The outdoor ageing is conducted continuously and only interrupted for the measurement of the LC's.

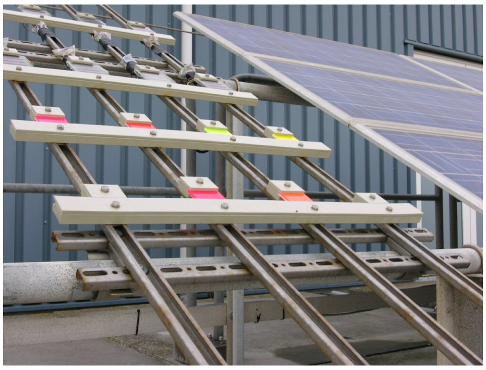

Figure 1: outdoor ageing setup at ECN, containing several LC plates.

During the ageing, the illumination is monitored in the plane of the LC using a pyranometer (CM21 from Kipp en Zonen).

Solar Test Facility (STF)

This indoor setup (STF from Solaronix SA) illuminates the LC's constantly with white light from a sulphur lamp of about 1/3 sun intensity, containing little to no UV light (see Fig. 2 for the sulphur lamp spectrum of the STF). Testing indoors gives an indication of the plate stability but a direct comparison with the outdoor experiments is not possible due to differences in light spectrum as well as the changing spectrum under outdoor conditions due to changing weather conditions. Furthermore it has been reported[12] that dye doped LC's show a recovery effect under outdoor conditions during low light illumination in the winter, which is not present in the indoor experiments.

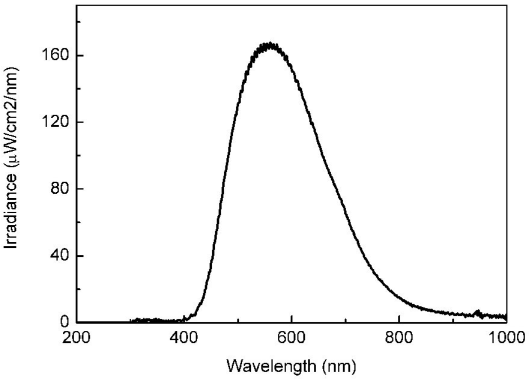

Figure 2: lamp spectrum of the sulphur lamp used for the indoor ageing experiments in the solar test facility (STF). The overall power of the lamp is 36,8 mW/cm^2, which corresponds to an intensity of about 1/3 of a sun.

Monochromatic light ageing (MLA)

This setup was developed by Solaronix SA to study the effect of "blue" and "amber" light, i.e. light that coincides with the absorption band of the CRS040 or RED305, on the stability of the LC's. The light source of this setup consisted of an array of monochromatic, high efficiency LED's to irradiate the LC's with wavelengths of 470 nm or 589 nm at the intensity of approximately 15, respectively 7.5 times the sun. To maintain constant and relatively low temperatures, the MLA setup was equipped with an integrated cooling system.

4 RESULTS

Figure 3(a, b, c) shows the absorption spectra of a LC doped with Red305. The spectra were taken at various intervals during illumination in the STF setup as well as under outdoor conditions. Also shown are the absorption spectra of a reference plate that was stored in the dark. As can be seen, Lumogen F RED305 from BASF seems to be quite stable in these plates. The reference shows no degradation and in the STF and outdoor setup, only minor bleaching of the dye is observed. At the same intervals, EQE spectra were taken. The result is shown in

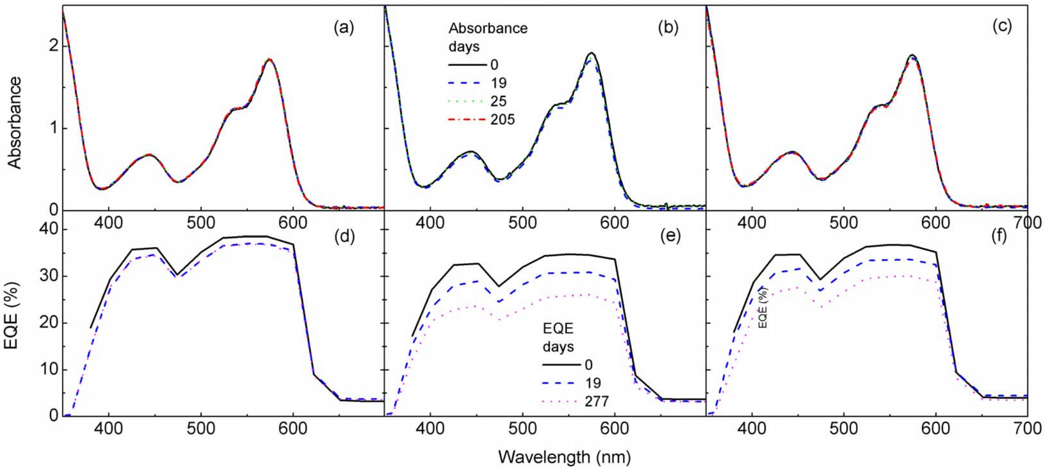

Figure 3: Absorbance (a ,b, c) and External Quantum Effficiency (d, e, f) spectra of RED305 doped LC plates, taken at various intervals during (a, d) storage in the dark, (b, e) continuous illumination under a suphur lamp, and (c, f) outdoor conditions.

Fig.3(d, e, f) The shape of the EQE spectra remains more or less unchanged. For all these spectra, the corresponding short circuit current (I_{sc}) was calculated by integrating the overlap of the EQE with the AM1.5G spectrum. These calculated currents were then normalized to the currents at the start of the experiments, i.e. before illumination. As shown in Fig. 4, the reference plate shows no or only minor degradation, whereas the plate aged in the STF setup and under outdoor conditions shows a decrease in I_{sc} of about 20%. The decrease in the STF seems to be faster than under outdoor conditions, but one has to keep in mind that the in the STF setup the illumination is continuous, whereas outdoor a day/night cycle is present. Despite the fact that no change in absorption is observed during illumination, the EQE, and thus the I_{sc}, does show a decrease. This means that the dye is absorbing the same amount of light, but less light is reaching the solar cell, either due to a reduction of the luminescent quantum efficiency of the dye or due to an increased loss of the emitted light on its way to the solar cell. The latter has been observed by Seybold *et.* al[11] for perylene dyes. Within the measurement error, the absorption measurements on RED305 do not show an increase in the absorption in the emission range of the dye. However, due to the long path length of the emitted luminescence before it reaches the solar cell, a small increase in absorption can lead to a noticeable reduction in EQE. From this it can not be concluded which of the two processes is responsible for the reduction in EQE.

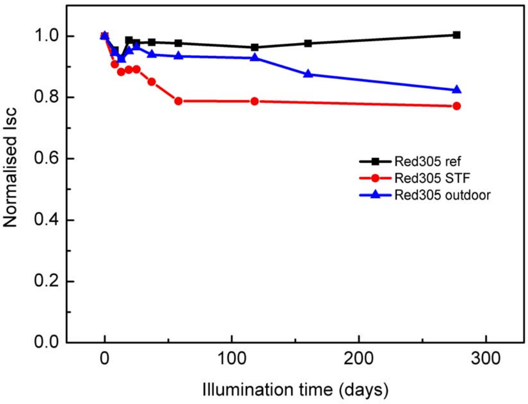

Figure 4: Calculated Isc at various intervals during ageing.

Because RED305 captures only a small region of the solar spectrum it is combined with the blue absorbing dye CRS040. LC’s doped with both RED305 and CRS 040 show higher initial power conversion efficiencies, 2.8% versus 2.5% for RED305 only, due to the additional light capturing of CRS040. Figure 5 shows the absorption spectra of a CRS040 and RED305 doped LC plate during the ageing. The reference plate that was kept in dark is stable for the duration of the experiment, but the plate that was aged in the STF setup, shows severe bleaching in the spectral range between 350 nm and 500 nm. This is the region where CRS040 is absorbing. The absorption band of RED305 between 500 nm and 600 nm remains almost unchanged, apart from a small decrease in the spectrum due to the disappearing absorption tail of CRS040. EQE spectra for this LC plate (see Fig. 6) also show a large initial decrease, followed by a small change in spectral shape. Based on the absorption spectra, this decrease is attributed to bleaching of the CRS040 dye, as the absorption of RED305 remains constant. Between 22 and 42 days of ageing, the shape of the EQE changes from the combined EQE spectrum, with a relatively high blue response and no dip around 475 nm, to the spectrum of a pure RED305 doped LC (compare with Fig. 3), showing that CRS040 has bleached almost completely.

For comparison a LC doped with only CRS040 was aged simultaneously. The absorbance spectrum of this LC plates reduced in 46 days to about 50% of the initial absorbance during the ageing. This reduction in absorbance is comparable to the reduction seen in the plate with both CRS040 and RED305 demonstrating the instability of CRS040.

To study the mechanism of the degradation of the dyes in more detail, monochromatic light ageing experiments were performed. In these experiments, high

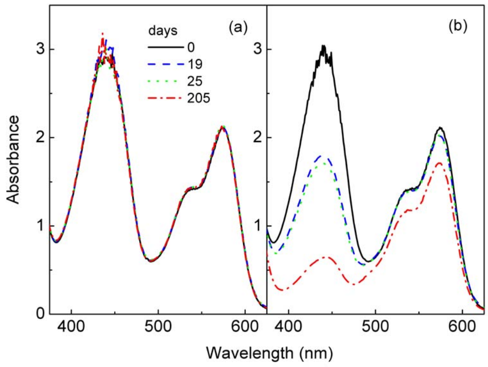

Figure 5: Absorbance spectra of CRS040/RED305 doped LC plates, taken at various intervals during (a) storage in the dark, (b) continuous illumination under a suphur lamp.

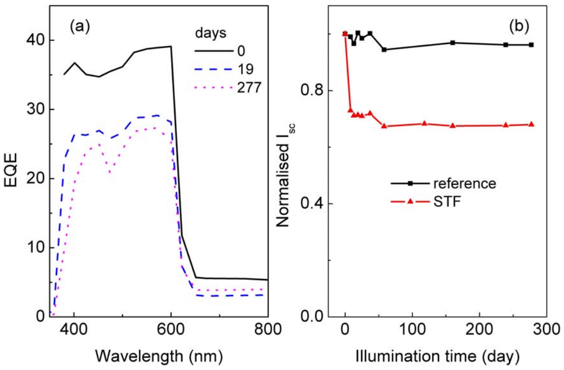

Figure 6: External Quantum Efficiency spectra (a) and calculated normalized Isc at various intervals during the ageing experiments.

intensity LED light was used to illuminate the LC plates only in the absorption band of one of the dyes. Figure 7 shows the effect of illuminating a RED305 doped plate at 470 nm, i.e. within the absorption band of CRS040, or 589 nm, corresponding to the absorption band of RED305. For both excitation wavelengths, the absorption of the plate remains unchanged after 631 hours of illumination. The same experiment was performed on a LC doped with both RED305 and CRS040. As can be seen in Fig 7, illumination at 589 nm does not induce degradation, but illumination at 470 nm induces severe bleaching of the CRS040 absorption band, as was also observed under white light illumination (see Fig. 5). Contrary to the general understanding that UV light is responsible for the bleaching of organic dyes, this experiment shows that bleaching of CRS040 is also induced by 470 nm light.

The results obtained above were compared with experiments on commercially available luminescent plates containing a similar dye as RED305. These plates showed a higher decrease in absorbance of 20% compared to 5% for the RED305 doped plate. However, the decrease of 20% in EQE is comparable. As the drop in EQE is the same as the decrease in absorption due to bleaching of the dye, it can be concluded that in the commercial plate the luminescent quantum efficiency of the dye remains constant, in contrast to the findings for the non-commercial plate. The difference could be due to the 20 times lower dye concentration in the commercial plate, or due to differences in matrix material.

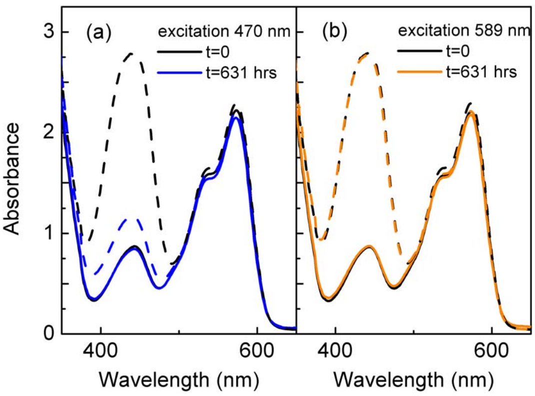

Figure 7: Absorbance spectra of a CRS040/RED305 doped LC plate and RED305 only doped LC plate before and after monochromatic light illumination at (a) 470 nm and (b) 589 nm.

5 CONCLUSIONS

Ageing experiments on Lumogen F RED 305 dye in LC plates show a marginal decrease in external quantum efficiency of about 20% upon continuous illumination by a white light source (1/3 of a sun; no UV) during 250 days, comparable to the decrease observed for commercial luminescent plates. Supplementing RED305 with a secondary dye, CRS040, improves the initial efficiency of the LC, but CRS 040 is found to be unstable. High intensity monochromatic light soaking experiments show that bleaching of the CRS040 dye is caused by excitation within its absorption band, contrary to UV bleaching. To substitute this dye, new dyes need to be considered, like e.g. Lumogen F Yellow 170 and Lumogen F 083 from BASF. These new dyes will be tested in a similar experiment.

5 ACKNOWLEDGEMENTS

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