# Fluorescence imaging: a powerful tool for the investigation of polymer degradation in PV modules

Jan Schlothauer, Sebastian Jungwirth & Beate Röder, Humboldt-Universität zu Berlin, Berlin, Germany, & Michael Köhl, Fraunhofer Institute for Solar Energy Systems (ISE), Freiburg, Germany

## ABSTRACT

This paper presents fluorescence detection as a new tool for the investigation of the degradation of EVA. The superior sensitivity of the setup contained herein allows an early assessment of the changes of the EVA after only 20 hours of damp-heat exposure. A newly developed scanning system allows the spatially resolved inspection of entire PV modules. Degradation of the encapsulants was detected after two years' outdoor exposure, as was the effect of cracks in c-Si cells, which coincide well with cracks made visible by electroluminescence.

### Introduction

Photovoltaic modules are designed to have a service lifetime of more than 20 years. Manufacturers normally specify the limit of the module's performance at the end of its life as 80% of the initial value [1]. While the majority of crystalline siliconbased modules produced during the last decades seem to meet these requirements, further cost reductions of PV are needed to successfully compete with traditional electrical power generation. Novel, less expensive materials and more cost-effective manufacturing must be introduced, but not to the detriment of the performance and durability of the final products. The performance-to-cost ratio and the integrity of the performance over the lifetime, namely, the total energy yield and the measure of durability, must be improved.

Service life testing of products that have a lifetime of a matter of decades is a challenge in itself. Accelerated life testing in the lab is required to simulate the passage of time, but the test procedures have to be validated via a comparison with real outdoor exposure testing. As material changes are closely linked to the performance of the module itself, sensitive methods for the detection of degradation-induced material changes – so-called degradation indicators – are urgently needed for an early recognition of ageing phenomena and the comparison of accelerated indoor with real-time outdoor testing. Electroluminescence has played this part, allowing for nondestructive observation of changes in the semiconductors and the other electrical Fab & Facilities

Cell Processing

Thin

Film

Ρν

Modules

Generation

Power

Market Watch

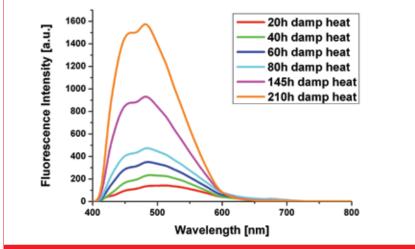
### **pco.edge** – the first camera system with the revolutionary sCMOS image sensor

Bringing to light! The new camera system pco.edge represents a perfect combination of high resolution, extremely low read out noise, and superior dynamic – at low NIR light (typical for electroluminescence), for excellent image quality even at high frame rates. Discover the new possibilities in the range of high performance applications. More information on www.pco.de/scmos-cameras/pcoedge/



- **EL** sensitivity
- high resolution
  5.5 megapixel
- readout noise
- < 1.4 electrons
- dynamic range
  > 22 000 : 1

imaging





parts of the module. However, degradation of the polymeric components of the modules remains a point of interest.

Ρν

Modules

Polymeric materials are used for the encapsulation of solar cells in order to provide protection against the environment and to buffer mechanical tensions caused by the daily temperature variations and the differences in the thermal expansion coefficients of the module components, mainly silicon and glass. The most common encapsulant is EVA (ethylene vinyl acetate), which can be found in various brands and grades (normal cure, fast cure, ultra-fast cure, etc.) on the market and in modules. The main differences between these brands and grades are their basic compositions (degree of vinyl acetate in ethylene), the per-oxide used for cross-linking during the lamination process, the additives used for stabilization against photo-degradation caused by UV-radiation and oxidation, and additives for processing. The degree of cross-linking of the EVA, usually measured as the gel-content after lamination, also depends on the lamination parameters like temperature and time. The back-sheet that is glued to the encapsulant usually consists of a stack of laminated foils, and plays the role of providing protection against the environment and controlling the water permeation into the encapsulant.

The most common methods for EVA degradation analysis are destructive methods like thermo-gravimetry, thermal analysis or transmission and reflection measurements [2]. These methods neither give information about the exact degradation process, nor are they suitable for an inline investigation of PV modules showing degradation before being visible or electrically measurable. Browning of the material is a degradation effect that is visible to the eye, but only after long-term operation close to the end of the service life. Results of long-term reliability and performance testing of PV modules have been published elsewhere [3]. Even though the various degradation mechanisms of EVA have been investigated for the last three decades, the ageing process under the influence of heat, humidity and UV radiation is not yet fully understood [4–7].

Previous studies conducted by Fraunhofer ISE investigated mini modules comprising one single cell. These mini modules were tested with different combinations of glazing, encapsulants and back-sheets which were exposed to various combinations of degradation factors including temperature, humidity and UV radiation, indicating the feasibility of fluorescence detection [8–10]. We also inspected seven commercially available PV modules with crystalline silicon solar cells and the traditional composition with EVA as encapsulant and a Tedlar/PET/ Tedlar back-sheet produced by different manufacturers with different material suppliers [3]. The modules had been exposed to two years' outdoor weathering at four different locations representing different climatic conditions: 1) Urban climate: Cologne, Germany; 2) Mountain: Zugspitze (2,650m), Germany; 3) Desert: Israel; 4) Tropic: Indonesia.

# Fluorescence as an indicator for polymer degradation

Fluorescence is a physical effect that may occur after a substance has absorbed light. In the case of so-called 'fresh' EVA, the probability of light emission after absorption is very low – this material can be considered to be non-fluorescent. Chemical changes occur as EVA ages, leading to the emission of a characteristic spectrum on excitement of the material by a suitable light source. The main thermal and photochemical degradation processes of EVA lead to the formation of conjugated polyenes and  $\alpha$ -,  $\beta$ -unsaturated carbonyl groups, which may show strong fluorescence.

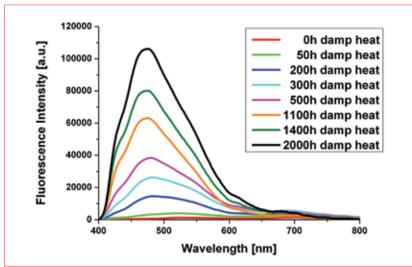
Laboratory investigations were conducted on mini modules as a modelling system for PV modules. A typical 90° geometry for measuring the fluorescence was chosen, while UV light of 375nm was used for excitation. The setup allowed the measurement of the fluorescence on single spots. The sample holder was suitable for positioning of  $10 \times 10 \text{cm}^2$  mini modules, which were aged under damp-heat conditions (85°C/85% r.h.). The exposure was interrupted for measurements from time to time. Six spots per module were measured and averaged.

The spectra of the mini module shown in Fig. 1 display the general behaviours of the measured fluorescence. The fluorescence intensity grows monotonically with increasing ageing time. It is clear from the image that signals are visible after times of only about 20 hours of accelerated ageing. The high sensitivity of the setup would even allow earlier fluorescence detection. A continuous growth of the signal was observed during test periods up to 2,000 hours (see Fig. 2), a common duration for service life tests. Fluorescence was detectable on any polymer encapsulant of the modules investigated so far. The results show the applicability of fluorescence detection as a method of assessment of the degradation of the polymer in a PV module [7,8].

# Scanning fluorescence spectroscopic imaging system

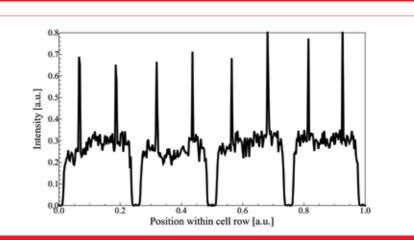
A scanning device was constructed to allow fluorescence spectroscopic imaging of complete PV modules. For commercially available module types, a total scanning area of about 2m × 1m is necessary. The height of the module varies within the range of a few centimetres, requiring a complete three-dimensional positioning system. A scanning concept was chosen to minimize negative effects of motion on the optics, consisting of a scanning head that is moved across the module parallel to the shorter side. The module is then moved line-by-line on a trolley parallel to its long side. The head contains a UV laser for excitation and the collection optics. Any detected light is guided via fibre optics to a stationary spectrometer. The positioning accuracy is substantially below the measurement spot size of about 1mm and the depth of focus.

The height of the scanning head can be adjusted for focusing with respect to the height of the construction frame and the module glazing. The tolerance is very comfortable, since the extension of the focus is bigger than the EVA thickness. The focus is adjusted in z-axis for maximum intensity over the whole module before starting the measurement. The laser excitation energy is adjusted for maximum dynamic resolution. Scanning is performed by moving the scanning head at constant speed. During scanning, the spectra are repeatedly collected with a constant integration time. The spatial coordinates are computed by taking into account the velocity of the



PV Modules







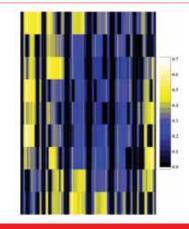


Figure 5. False colour image of the spatially resolved fluorescence intensity for module C2 (rows and/ or lines were clipped for anonymity reasons). The module was exposed to Indonesia's tropical climate for two years. The intensity is normalized, showing lower fluorescence at the centre of the module.

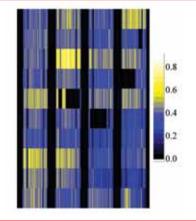


Figure 6. False colour image of the spatially resolved fluorescence intensity for module C3 (rows and/or lines were clipped for anonymity reasons). The module was exposed to a desert climate for two years. The intensity is normalized; peculiar spots appear on cells in lines 2 and 4 to 6 where the fluorescence on the cell disappears.



Figure 3. Illustration of the scan path across the PV modules.

scanner. For module analysis, only one scan per cell row could be performed for the investigations presented here because of time constraints. The scanning direction is alternated for every other cell row (see Fig. 3). A low scanning speed can be chosen for high resolution. As the fluorescence spectra were integrated yielding the total fluorescence intensity, the data are then translated into a false-colour image showing the spatial fluorescence intensity distribution. Because the colour scales are normalized and selected for best visibility for all following figures, the differences in the excitation energy must be computed separately for absolute intensity comparison.

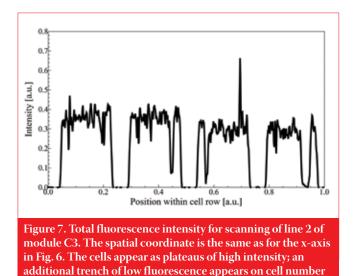
# Comparison of the fluorescence measurements of complete PV modules

Figs. 1 and 2 show the ageing timedependent fluorescence signal without spatial variation. Conducting measurements with spatial resolution on complete PV modules allows for the display of fluorescence intensity over the spatial coordinate, as shown in Fig. 4. Plateaus of high fluorescence intensity separated by trenches of low fluorescence intensity can be clearly distinguished. Spikes rising up from the plateaus spatially coincide with the position of the bus bars.

Several processes can be said to cause this spiking effect: excitation UV irradiation might be reflected by the bus bars yielding a higher fluorescence; the fluorescence itself may be reflected, explaining the strong signal increase; or there may be a real difference in the local condition of the polymer due to the bus bars.

The trenches of low fluorescence between the plateaus are significantly wider than the spacing of the cells. A general assumption could be made that this behaviour is caused by a diffusion process. The degradation products which normally seem to be fluorescent are then chemically altered into non-fluorescent species.

Combining all scanned lines of a module and translating the intensity into colours yields a complete image of the module. Fig. 5 shows the results of two years of outdoor exposure in Indonesia, indicating the occurrence of fluorescence across the entire module with a significantly higher intensity near the edges. Higher fluorescence



intensity on the cells is associated with higher degradation of the polymer.

Fluorescence imaging was performed for numerous modules [11,12]. Another module was selected to demonstrate the ability of the fluorescence analysis to evaluate distinctive features. Fluorescence intensity suddenly drops to a very low level on certain cells. This effect can be seen for several cells on the C3 module in Fig. 6, though no visible changes were apparent. A line scan illustrates the difference between fluorescence intensities on the cell and the peculiar spot for cell number four in line two (Fig. 7).

# Combination of fluorescence and electroluminescence

4 (right-hand side).

The distinctive features of cells with areas of low fluorescence were also investigated more thoroughly. The fluorescence imaging was performed at a higher resolution using 15 scan lines for one cell, acquiring approximately 500 spectra for each scan, for the investigation of the distinctive cell features. An electroluminescence (EL) image was taken to assess electrical peculiarities of this cell, the results of which are shown in Fig. 8. The electroluminescence image reveals a crack in the silicon wafer from the lower left end to the top centre. A clearly recognizable area of low fluorescence can be seen in the FL image all along the crack. The spatial correlation is quite apparent in the combination of the two images.

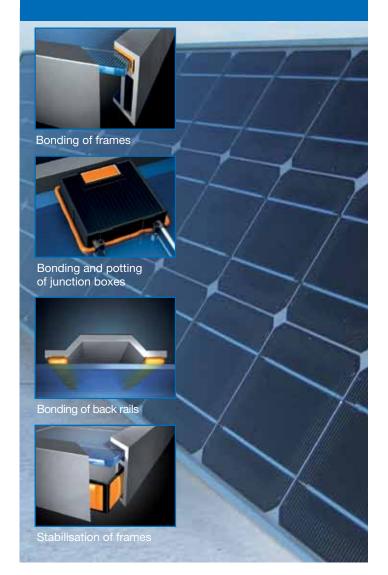
The width of the non-fluorescent area around the crack and the distance from the edge of the cell to the beginning of high fluorescence seem to be closely related. Assuming that diffusion can take place from the side of the module and through the crack in the silicon wafer in a similar manner, such a process may be causing the bleaching of the fluorescent species.

Taking a closer look at Fig. 9, strong browning is visible on a module following outdoor exposure at the Joint Research Centre (JRC) in Italy for an extended period of time. The browning on the cells has reached a state which normally should not occur during the service life. The fact that the browning is visible to the naked eye indicates that the polymer is being tested at a very late stage. A bleaching of the colorant species occurs around the cracks in the cover glazing. It can be assumed that similar processes of diffusion through cracks in the wafer and in the glazing are the reasons behind the bleaching in the browning image (Fig. 9) and in the fluorescence image of Fig. 8.

## Conclusions

Fluorescence detection can be a sensitive and non-destructive method for the investigation of the degradation of the encapsulant polymer, EVA in this case. Changes in the fluorescence can be closely tracked, from directly after production until an ageing state resulting from damp-heat testing of more than 2,000 hours.

# Photovoltaic modules perfectly sealed and bonded

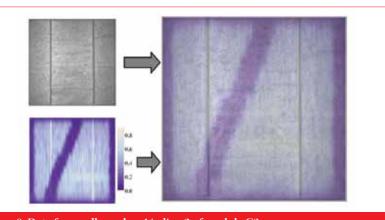


Sealants, adhesives and encapsulants are only a minimal expense factor in photovoltaic modules. But they have a considerable influence on the life time and on the durability of the photovoltaic module against climatic influences. Applying the premium products of OTTO ensures you to benefit from more than 40 years of expert knowledge.

#### **OTTO – always a good connection!**

Hermann Otto GmbH 83413 Fridolfing • Germany Phone: 0049-8684-908-0 pv@otto-solar.com www.otto-solar.com





### PV Modules

Figure 8. Data from cell number 4 in line 2 of module C3. Top left: electroluminescence image. Bottom left: fluorescence intensity image in false colours from dark blue to white. Right: overlay of the fluorescence image over the electroluminescence.

Spatially resolved fluorescence spectra are collected for complete modules, and in the future this may also occur at high resolution. The total fluorescence intensity gives the first information about the local polymer degradation. Complex spectral information has the ability to provide much more information about ageing processes. The fluorescence can be used as an indicator from a very early stage regarding the ageing state of the polymer. Differences in the spatial distribution of the fluorescence over modules can be seen, leading to the assumption of spatially inhomogeneous ageing.

Fluorescence and electroluminescence are strongly correlated in the vicinity of cell cracks. This paper showed that a diffusion process takes place around cracks either in the glazing or in the wafer affecting the local fluorescence intensity. In the case of the presented modules, a bleaching was visible in the defined area around cracks.



Figure 9. Photograph of a module after extended outdoor exposure at JRC (Italy) showing strong browning caused by photo degradation of the EVA and bleaching effects around the cracks in the cover glass. (This module is unrelated to other modules investigated in this project.)

### Acknowledgements

This work was supported by the BMU (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety), under the project title: Reliability of Photovoltaic Modules, FKZ 0329978A. The authors would like to thank Steffen Fahnauer and his colleagues from the

mechanical workshop of the Humboldt-Universität for their excellent support in building the scanning equipment.

#### References

- [1] Wohlgemuth, J.H. et al. 2006, "Long term reliability of photovoltaic modules", *Proc. 4th World Conference on PV Energy Conversion.*
- Marín, M.L. et al. 1996, "Thermal degradation of ethylene (vinyl acetate) – Kinetic analysis of thermogravimetric data", *Journal of Thermal Analysis*, Vol. 47, pp. 247–258.
- [3] Herrmann, W. et al. 2010, "Results of a German four-year joint project -Part II, results of three years module weathering in four different climates", *Proc. EU PVSEC*, Valencia, Spain.
- [4] Allen, N.S. et al. 2001, "Aspects of thermal oxidation, yellowing and stabilization of ethylene vinyl acetate copolymer", *Polymer Degradation and Stability*, Vol. 71, pp. 1–14.
- [5] Pern, F.J. & Czanderna, A.W. 1992, "Characterisation of ethylene vinyl acetate (EVA) encapsulant: Effects of thermal processing and weathering degradation on its discoloration", *Solar Energy Materials and Solar Cells*, Vol. 25, pp. 3–23.
- [6] Pern, F.J. 1997, "Ethylene vinyl acetate (EVA) encapsulants for photovoltaic modules: Degradation and discoloration mechanisms and formulation of improved photostability", *Die Angewandte Makromolekulare Chemie*, Vol. 252, pp. 195–216.
- [7] Allen, N.S. & Edge, M. 1994, Fundamentals of polymer degradation and stabilisation, Elsevier Science Publishers Ltd., Essex, UK.
- [8] Röder, B. et al. 2008, "Observation of polymer degradation processes in photovoltaic modules via luminescence detection", *Proc. SPIE*

Vol. 7048.

- [9] Jungwirth, S. et al. 2010, "The influence of different back sheet materials on EVA degradation in photovoltaic modules investigated by luminescence detection", *Proc. SPIE-Conf.* 7773.
- [10] Röder, B. et al. 2010, "The influence of different ageing factors on polymer degradation in photovoltaic modules investigated by luminescence detection", *Proc. SPIE-Conf. 7773.*
- [11] Röder, B. et al. 2010, "Investigation of outdoor degradation of photovoltaic modules by luminescence and electroluminescence", Proc. SPIE-Conf. 7773.
- [12] Röder, B. et al. 2010, "Combined luminescence and electroluminescence as powerful tool for the inspection of polymer degradation in photovoltaic modules", *Proc. EU PVSEC*, Valencia, Spain.

#### About the Authors

**Beate Röder** studied biophysics at the Gorki-University in Kharkov (Soviet Union). Since 1993 she has had a professorship in experimental physics at the institute of physics at the Humboldt-Universität zu Berlin. In 2007, she began the investigation of luminescence as a method for non-destructive detection of polymer ageing processes. Her main area of interest is the detection of extremely low light fluxes.

Jan Schlothauer and Sebastian Jungwirth, both attending Humboldt-Universität zu Berlin, studied physics and began working on their Ph.D. theses on the theme of ageing processes of polymer encapsulants in PV modules under the supervision of Beate Röder in autumn 2009.

Michael Köhl, physicist, has been working in the field of development, characterization, analysis and service life testing of components for solar applications since 1977. Recently, his main focus has been on the durability of PV modules as he has taken the role of coordinator of the German 'PV-reliability' project and of Subproject 5 'Lifetime assessment of PV modules' within the EU-funded 'Performance' project.

#### Enquiries

Dept. PV-Modules, Systems and Reliability Fraunhofer-Institut für Solare Energiesysteme (ISE) Heidenhofstr. 2, 79110 Freiburg, Germany

Tel: +49 761 4588 5124 Fax: +49 761 4588 9124 Email: michael.koehl@ise.fraunhofer.de Web: www.ise.fraunhofer.de