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Degradation of the encapsulant polymer in outdoor weathered photovoltaic modules: Spatially resolved inspection of EVA ageing by fluorescence and correlation to electroluminescence

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ABSTRACT

Here we report about the use of spatially resolved fluorescence spectroscopy for non-destructive analysis of encapsulants in outdoor weathered commercial PV modules. Photovoltaic modules with crystalline Si-cells of seven German manufacturers were analyzed after 2 years outdoor weathering in four different climates. For the first time spatially resolved images of the polymer fluorescence for complete photovoltaic modules are reported.

The presented results show that the fluorescence intensity and distribution is inhomogeneous within any module. The fluorescence intensity and its spatial distribution depend on the climate, particularly the weathering site. Diffusive processes in the polymer layer between glass and silicon cell can be evaluated with this method. Cracks in the wafer, visible with electroluminescence, show up in spatially resolved fluorescence images as well. The diffusion through the cracks influences the spatial distribution of the fluorescence intensity.

Compared to averaging methods, detailed information about the impact of the different degradation factors like UV-irradiation and moisture ingress on the degradation processes can only be obtained using spatially resolved fluorescence measurements. For PV-modules investigated in this study areas can be identified and compared where similar degradation parameters can be assumed. This will allow improving to quantitatively interpret measurement results.

1. Introduction

Manufacturers of photovoltaic (PV) modules give warrantees for their products assuring the efficiency will not drop below 80% of its initial value during service life. Current warranted service life of PV modules from German manufacturers ranges from 20 to 25 years. This is quite long considering that terrestrial solar power is exploited by photovoltaic only within the past 40 years [1]. To justify these long-term warrantees it is necessary to predict the lifetime of the products. Since real life testing is out of the question for a reasonable time to market, accelerated testing is needed to ensure that the use of novel, less expensive materials and more cost-effective manufacturing does not spoil the durability of the products. This puts high demands on the ability to conduct accelerated testing and relate results obtained by these tests to real life conditions. Obtaining suitable models for durability tests is a major goal to evaluate the effect of new developments on the lifetime of the product. It should be emphasized, that terms such as durability/reliability/life/lifetime are not consistently defined in literature and point to a discussion, i.e. in [2,3]. Qualification test sequences, such as those according to IEC standards, have become a pass/fail indicator whether the product is qualified for sale. However, qualification testing is not a method for a quantitative prediction of the products service life in general [2,4].

Accelerated ageing methods are used to mimic climate effects and are employed for qualification testing in defined sequences. In real life however, all degradation mechanisms influence the life of a PV module. Accelerated ageing, such as damp-heat (i.e. 85 °C/85%.r.h.) and UV-irradiation, combined with mechanical stress and other effects, such as corrosive atmosphere, etc. add to degradation and in combination with each other form a complex field of influencing factors. Identifying and isolating parameters from real life testing which allow early assessment of the product and which can be related to accelerated testing procedures will greatly improve the accuracy of the predicted life from accelerated testing.

Many of the investigations to evaluate the degradation of PV modules focus directly on efficiency-related parameters to assess

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the electrical condition of the module, such as *IV*-curve measurements, electroluminescence, thermo-imaging or more sophisticated techniques [2,5,6]. However, modules are usually of such good quality, that these parameters vary only little with time at the beginning of the exposure to natural or artificial weathering. Investigating the mechanism causing degradation of the components in a PV module is an approach to get information about the degradation progress before the electrical properties are influenced. The most interesting component in this respect is the encapsulating polymer which has to protect the electrical parts such as the wafers and electrical connections which are embedded within.

The most widely used encapsulation material for PV modules is ethylene vinyl acetate (EVA). Many studies have been conducted, utilizing destructive methods like thermogravimetry, thermal analysis, strain testing or NMR to assess the conditions of the EVA. Such mechanical or chemical analyses require the destructive extraction of samples of the polymer from the module. These methods provide insight into the condition of the EVA down to the molecular level but they are not suitable for an in-line or in-the-field investigation of PV modules. Optical methods play an important role in determining the polymer degradation. Methods such as transmittance spectroscopy, FTIR spectroscopy or Raman scattering were applied to samples of EVA, either produced for this type of measurement or destructively taken from a module. Various degradation mechanisms of EVA have been investigated within the last three decades. Ageing caused by heat, humidity and UV radiation induce many competing processes and form a complex field of influencing parameters [3,6–10]. The usage of additives such as UV light stabilizers, UV absorbers and antioxidants in EVA sheets for PV application improves the EVA stability significantly [11]. These additives and also traces of curing agents or polymerization catalysts influence the effect of the environmental conditions; some may even cause new ageing effects due to degradation of the added component [12]. Volatile compounds such as acetic acid and hydro-peroxides are formed [8]; the presence of acetic acid is known to catalyze the degradation itself thus affecting other degradation mechanisms [13].

Some methods also facilitate non-destructive investigation of the ageing of the encapsulation polymer in a PV module. By visual inspection of outdoor weathered modules a discoloration can be noticed. For quantification of this effect the yellowness index is utilized. This parameter, however, develops comparably slow with time. PV modules currently in the market show no visible yellowing for many years of operation in moderate climates. Towards the end of service life the extent of yellowing can lead to losses in PV module energy output [14].

Fluorescence spectroscopy is a sensitive method to detect decomposition products (chromophores), even before they become visible. Thorough investigations of samples of encapsulation materials, especially EVA, were conducted by Pern et al.; many findings are compiled in [3]. The discoloration is due to several degradation mechanisms, leading to the formation of chromophores within the polymer. From the thermal and photochemical degradation processes of the EVA the formation of polyenes and α,β-unsaturated carbonyl groups was shown to cause discoloration and fluorescence. Additives used for curing or stabilization degrade, causing fluorescence as well [15–17].

The investigations by Pern et al. give rise to the assumption that the ratio of the influence of the several ways of degradation of the polymer in modules varies, when accelerated ageing is conducted at different temperatures. Ageing at temperatures at or above 105° (in combination with UV) generates additional degradation effects in components such as the back sheet compared to common ageing condition such as 85 °C. The reported browning patterns of highly accelerated UV ageing even show inverted effects compared to those observed after outdoor weathering [15,18,19]. These findings suggest that further reaction paths can be triggered by higher temperatures. Flame retardant properties of EVA were investigated, using temperatures up to 500 °C [20]. However, it cannot be expected, that these results allow quantitative predictions of the outcome of outdoor weathering of PV modules. Nevertheless, some degradation paths, such as the formation of polyenes were observed, when using temperatures up to 400 °C [20], after ageing at 180 °C in hot air however, this degradation path was not found to be significant [8]. For these reasons we have to behave cautiously, when comparing EVA degradation parameters if the accelerated ageing conditions vary over a wide range.

When comparing published results from fluorescence spectroscopy, several other factors besides the ageing conditions must be considered. The chosen excitation or emission wavelength influence the type of formed and the selection of detected chromophores. Spectra obtained by synchronous scanning fluorescence spectroscopy cannot be compared directly with emission spectra. Since luminescence investigations show a broad excitation band around 370 nm, fluorescence emission spectra excited at wavelengths of 350–380 nm are considered comparable in a general sense [21].

Several mechanisms affect the fluorescence intensity in a complex way. In the presence of oxygen and under the influence of temperature and UV light the fluorescing species may be oxidized further, diminishing the fluorescence. These effects may be localized especially when diffusion (of oxygen e.g.) is a rate-dominating factor in these reactions [3].

Non-destructive investigations, with fluorescence spectroscopy without spatial resolution and averaging over several points on the sample, were conducted on mini-modules, build equal to commercially available PV modules, encapsulated with EVA, but comprising only one cell [22]. The mini modules were aged in a climate chamber. The exposure was frequently interrupted for the fluorescence measurements. These investigations showed that the fluorescence intensity increases with Damp/Heat (DH) ageing duration [23]. It was found that the fluorescence response to accelerated ageing is different for different encapsulation materials. Also different accelerated ageing procedures and back sheet materials have influence on the fluorescence spectrum and the integral intensity [22]. For the investigated samples DH and UV ageing could be clearly distinguished by characteristic differences in the spectrum. An interaction between DH and UV ageing was found. Some fluorescent species caused by UV ageing were bleached during the following DH ageing.

Here we employ the method of fluorescence detection to take spatially resolved images of complete PV modules. We report the results of the inspection of commercially available PV-modules after two years outdoor exposure in four different climates. The most important factors for polymer ageing can be determined for the different climatic conditions by comparing the ageing effects of these modules.

2. Experimental

2.1. Samples and exposure

The examined modules are crystalline Si-PV modules produced by seven German manufacturers with their own (some which may be replicates here) material suppliers [6]. All modules have a comparable construction, consisting of solar glass, EVA encapsulation, polycrystalline or monocrystalline Si cells and a Tedlar/PET/Tedlar back sheet. Data presented here are anonymized and, when necessary, information is reduced to show the general effect.

The modules were exposed to 2 years outdoor weathering at four different locations representing different climatic conditions: