Corrosive effects of ammonia on PV modules and their evaluation

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ABSTRACT

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Ammonia, a gas which has its roots in livestock farming, can have potentially detrimental effects on the lifetime and reliability of PV modules. Research into the degree of corrosive effects of this gas on modules is of utmost importance for any module manufacturer guaranteeing a certain specific lifetime for their product. Researchers from SCHOTT and SCHOTT Solar together with the DLG (Deutsche Landwirtschafts-Gesellschaft/German agricultural society) developed a test design involving humidity, temperature and ammonia gas. This design is based on permeation testing and microscopic analysis of samples aged under a controlled atmosphere or from outdoor exposure. Additionally, a highly accelerated test is presented which allows screening materials for use in PV modules within 84 hours. An Arrhenius type of model is used to calculate the acceleration factors involved. Based on this model, the proposed test design is equivalent to more than 20 years of outdoor exposure in the rural environment (in Central Europe).

Introduction

The agricultural environment in Central Europe represents a substantial market segment for the application of PV modules (e.g. 19% of all investors for PV systems in 2009 in Germany [1]). Although this has been threatened of late as a result of the German government's cutting of the feedin tariff for free-standing PV applications on agricultural land, the assessment of the specific risks for reliability and lifetime expectancy of PV modules in the agricultural environment is still crucial. A variety of potentially harmful gases - such as ammonia, carbon dioxide, methane, hydrogen sulphide and nitrous oxide - can emanate from livestock farming (e.g. pigs, cows or chickens) [2]. Two of these gases are potentially corrosive (ammonia and hydrogen sulphide); the others are what have become known as greenhouse gases.

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Ammonia can be identified as being more relevant than hydrogen sulphide with respect to degrees of corrosive damage inflicted. The maximum workplace concentration value of ammonia is higher (20ppm vs. 5ppm) and it forms strong bases, whereas hydrogen sulphide forms a relatively weak acid (comparable to carbon dioxide, whose atmospheric concentration is 350–400ppm).

In other environments, different gases may need to be considered – for example, in the vicinity of volcanoes, gases like CO_2 , SO₂, H₂S, HCl or even HF may result in a more significant corrosive attack [3]. Similarly, near fossil fuel burning sites (including motorways and railway trails), other potentially corrosive gases prevail (e.g. SO₂, NO_x, CO₂). For each of these environments, a corresponding approach – as for ammonia in this paper – would need to be taken if identified as a significant area of PV application.

Regarding field data, not much is known of specific damages occurring to PV modules in the rural environment; however, one severe case of the loss of adhesion of a junction box and a subsequent arcing is reported by Althaus et al. [4], which can most likely be attributed to the system's being installed above a pig pen exhaust outlet. The same publication reports the browning of an adhesive and the corrosive attack of the aluminium frame due to ammonia exposure [4]. Ammonia is known to induce minor damage in metals such as silver and aluminium, and to severely attack several polymer materials such as PET, PBT and PC [5]. Therefore, the loss of adhesion of a polymer is likely to be attributed to the influence of ammonia gas. These data highlight the importance of assessing ammonia resistance for PV modules, both as a prerequisite for warranting stability of power output as well as for security reasons.

Experimental approach

In order to assess the influence of ammonia on photovoltaic modules, a systematic approach is needed to describe the diffusion behaviour of ammonia within a PV module while outlining the main damage mechanisms that result from the presence of ammonia in combination with humidity. For a valid correlation of test conditions with outdoor exposure, knowledge of the temperature dependence of both aspects is required.



Figure 1. Setup for highly accelerated ammonia life test. The desiccator was filled with an ammonia solution designed to produce an ammonia concentration of 50,000ppm at 85°C, as well as various materials used in PV modules, such as glass/EVA laminates, cables etc. that do not come into contact with the liquid ammonia solution.

This study proceeded to determine the permeation of ammonia through a major encapsulant material (ethyl vinyl acetate, EVA) as well as a major back sheet material (Tedlar*/PET/Tedlar* (TPT)), allowing the evaluation of the temperature dependence. In order to identify the main damage mechanisms, PV modules were mounted in a test chamber with ammonia concentrations up to 2,000ppm in 70°C/70% relative humidity for a total duration of 840 hours. These PV modules were characterized together with a module from the roof of a pig pen which had been operating outdoors without problems for four years. Additionally, module components such as glass and encapsulation materials were stored in a highly accelerated ammonia life test, which consisted of ammonia concentrations of 50,000ppm at a temperature of $85^\circ\mathrm{C}$ and 100% relative humidity for a time of 84 hours (see Fig. 1).

Ammonia diffusion

The transmission rates of ammonia gas through EVA and TPT were evaluated at different temperatures. The transient data were analyzed according to the approach proposed by Kempe [6], from which diffusion and solubility constants can be extracted. The TPT laminate was considered as a homogeneous material, since the Tedlar layers are comparably thin and it can be assumed that the obtained values reflect the properties of the central PET layer. The aim of this analysis was to estimate the times for ammonia ingress into a photovoltaic module.

Results of the diffusion and solubility constants of the two relevant polymer components are shown in the graph in Fig. 2. The solubility constants are similar for the two materials and depend only weakly on temperature. The diffusion constants are two orders of magnitude higher for EVA than for TPT. The ammonia ingress times into a PV module can be estimated from these data, according to the formula for the average range x_{av} of the entering gas:

$$x_{av} = \sqrt{Dt} \tag{1}$$

when *D* is the diffusion constant and *t* the time. Fig. 3 displays times for ingress into a typical PV module, where 1mm is representative of a typical EVA thickness, and 76mm is half the size of a 6" cell.

These data imply that in the field, ammonia penetrates the outer skin of an EVA/TPT PV module within a few days. Although it can take several years to reach the centre of the cells at the front side, corrosive effects – if present – can begin immediately after deployment near the rims of the cells. On the other hand, a test design for ammonia resistance should take the time lag into account (typically a few days) which can retard the ammonia action within the PV module.

The situation is different for 'double glass' modules that have a back-side glass slide instead of a polymer foil or laminate. Ammonia is unlikely to penetrate at all within these modules; if it does so, it would be from the rim. In such a scenario, a comparably thick polymer sealing (at least several millimetres) and a certain distance of the cells from the rim (again, several millimetres) must be ensured, thus delaying any corrosive attack until much later in these modules' lifetimes.

Damage mechanism: glass corrosion

The modules were extracted from preliminary ammonia tests and outdoor exposure and inspected by light microscopy and scanning electron microscopy (SEM) and energy-dispersive x-ray detection, paying particular attention to the metallization features of the solar cells (bus bars, fingers and back contacts) and interconnectors.



Figure 2. Diffusion and solubility coefficients of ammonia in EVA and TPT, with the latter evaluated as a single material. Graph lines are Arrhenius fits to the data (activation energies $E_A = 17.2 kJ/mol$ for the diffusion coefficient of EVA and $E_A = 32.5 kJ/mol$ for TPT (PET)).

No signs of degradation were observed. Therefore, more detailed investigations concentrated on the front glass and the polymer components of the module.

After ammonia tests with the modules, light microscopy and white-light interference microscopy of the front glass showed locally minor damage to the glass surface in the nm range (see Fig. 4). Modules that had undergone four years of outdoor exposure showed no such signs (see Fig. 4). The signs of glass corrosion were not unambiguous, however. The front glass was subjected to high ammonia load conditions (50,000ppm) which led to severe glass damage in the form of an extreme surface roughness and the formation of a film of crystallite-like particles which could not be wiped away using either water or ethanol (for details see [7]). These are typical signs of severe glass corrosion [8], which strongly suggests that this is an area of potential damage as a result of the presence of ammonia.



Figure 3. Ammonia ingress times for different distances in materials, extrapolating the value for TPT/PET at 23°C.



 \times 47µm) of PV module front glass after preliminary module tests (up to 2,000ppm ammonia at 70% humidity and 70°C for 840 hours) and outdoor exposure (four years on top of a pig stable roof).

As the outdoor-exposed module from the pig stable did not show any signs of front-glass corrosion, realistic field conditions do not seem to implicate a significant damage of the module front glass. The situation is, however, very different in the case of antireflective-layercoated (ARC) front glasses, as the visual appearance of such modules could degrade much more severely due to glass corrosion.

Glass corrosion results from the fact that ammonia forms a base according to the following reaction:

$$NH_3 + H_2O \iff NH_4^+ + OH^-$$
 (2)

The degree of degradation is related to the concentration of hydroxyl ions, *c*(*OH*⁻),

which may be assumed to be proportional to:

$$c(OH^{-}) \propto \sqrt{c(NH_3)c(H_2O)}$$

where $c(H_2O)$ and $c(NH_3)$ are the water (vapour) and the ammonia concentrations, respectively.

(3)

Soda-lime glass is currently being used as the front glass material by the vast majority of PV module manufacturers (as is the case for ARC glasses). Therefore, glass corrosion is expected to be a prevalent feature. Glass corrosion of sodalime glass in an alkaline environment is mediated by the hydroxyl ion through the disruption of siloxane bonds [9]. In order to model glass corrosion depending on ambient conditions, the corrosion rate



with and without a highly accelerated ammonia life test (50,000ppm ammonia).

 r_{glass} may be assumed proportional to the hydroxyl ion concentration with an Arrhenius dependence on temperature:

$r_{glass} \propto exp(E_A^{gl} / K_B T) \cdot \sqrt{c(NH_3)c(H_2 O)}$ (4)

For the activation energy E_A^{gl} of glass corrosion in alkaline solutions, a value of 158kJ/mol has been determined [10]. However, the temperature dependence of ammonia-induced glass corrosion of glass-lined steels may be described by an activation energy closer to that observed in the acid-driven corrosion of soda-lime glasses, namely 79kJ/mol [11,12]. Both values are quite high and implicate a large acceleration in terms of increasing the temperature for an accelerated lifetime test.

"Glass corrosion of soda-lime glass in an alkaline environment is mediated by the hydroxyl ion through the disruption of siloxane bonds."

Therefore, any accelerated test will increase the glass-corrosion damage much more significantly than other mechanisms with lower activation energy. As a result, it becomes clear why samples from accelerated ammonia tests (as that discussed above) show signs of glass corrosion whereas outdoor-exposed samples do not (as in Fig. 4). The same applies, incidentally, to the classic damp heat test, where a disproportionate acceleration of front glass corrosion should also be expected (however, an acid-driven leaching of the surface is more likely in this case).

Damage mechanism: polymer degradation

Several polymer components of PV modules as used by SCHOTT Solar were subjected to highly accelerated ammonia life test (50,000ppm/85°C/100% relative humidity/84 hours). Attenuated-totalreflection infrared (ATR-IR) analysis of the respective materials did not show major degradation of any material investigated, which included cables, the junction box, adhesives and back-sheet materials. Minor modifications were noticed in the ethylene vinyl acetate copolymer used for encapsulation. As shown in Fig. 4, although the main peaks do not change, a small peak around 1,795cm⁻¹ disappears upon ammonia treatment, both for cured and for uncured material.

This peak is very likely a signature of the C=O double bond as it is shifted versus the main C=O peak of vinyl acetate $(1,735 \text{ cm}^{-1})$. As a result, the peak is assumed to be associated with an additive, possibly a peroxy esther which may be

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used as a curing agent. The respective chemical compound degrades in the highly accelerated ammonia life test.

From the experimental findings, degradation of polymer components may be identified as additional potential failure mechanisms brought about by the presence of ammonia. The environment most likely to result in the activation of the degradation mechanism of polymers in ammonia (i.e. alkaline) is the saponification reaction, i.e. the hydrolysis of an ester to form an alcohol and the anion of a carboxylic acid. This can occur in ethylene vinyl acetate copolymers and their additives as well as in other polymer components of the module. The disappearance of the 1,795cm⁻¹ peak in the IR spectrum of the encapsulant material (see Fig. 4) might be a signature of this type of reaction - presumably only for an additive and not for the polymer backbone. Similar to glass corrosion, the saponification reaction is mediated through hydroxyl ions. Therefore, the dependence of the respective degradation rate r_{polym} may be assumed to be similar to equation (4):

$r_{polym} \propto exp(E_A^{po} / K_BT) \cdot \sqrt{c(NH_3)c(H_2O)}$ (5)

The activation energies of different types of saponification reactions range between 40 and 42kJ/mol [13].

Test designs

Various norms can be found for corrosion testing of products by corrosive gases like H₂S, NO₂, Cl₂, and SO₂ (DIN EN 60068-2-60), or by SO_2 with a cyclic temperature program (DIN EN ISO 3231, ISO 6988-1985 and DIN 50018). DIN 50916:1985 is presumably the only norm referring to a test with ammonia (generated by an NH₄Cl-NaOH solution with defined pH); it is designed to test stress-corrosion cracking of parts made of copper alloys. No explicit norm is available for the corrosion testing of PV modules subjected to ammonia; however, an international standard is currently under development (Ammonia corrosion testing of photovoltaic (PV) modules, 82/600/ NP). Some module manufacturers claim to pass an ammonia test according to DIN 50916:1985.

Various designs for testing the impact of ammonia atmosphere on PV modules have been proposed of late, some of which are listed in Table 1. In the DLG test centre, a test design was proposed for best comparison with a reference scenario taking the ammonia ingress times and the different degradation mechanisms into account. Other proposed tests involve cycling conditions between elevated temperatures (40°C as in ISO 6988-1985 or 45°C) and room temperature. Table 1 outlines details of these test conditions. The highly



accelerated ammonia life test developed at SCHOTT (HAALT) is also included (Test design no. 4); the respective conditions can, however, only be applied to small components (cells, polymers...) because the duration required for ammonia ingress into a complete PV module would introduce a too long a time lag.

These different test designs may be compared to a reference scenario of 20 years of outdoor exposure. The following conditions were assumed as typical of Central Europe: an average temperature of 12°C, an average relative humidity of 80%, 1,000 hours of direct sunshine with an assumed module temperature of 60°C [14], and, as a 'worst case' scenario, an ammonia concentration of 50ppm. This ammonia concentration is the maximum value occurring in livestock stables [15]; a similar value (46ppm) was reported by Althaus et al. [4]. In Germany, 20ppm is the maximum value permitted by the official regulatory bodies [16].

"Test designs #3 and #5 clearly fail to reach equivalence to the reference scenario within a reasonable test time."

Fig. 6 depicts calculated times for which the different test designs have reached an equivalent degradation status to the reference outdoor scenario. The three values reflect the equivalence with respect to glass corrosion (Equation 4), polymer degradation (Equation 5, cf. Figs. 2 and 3) and diffusion within EVA, respectively. The DLG test design (#1) with a duration of 1,500 hours therefore relates to realistic outdoor conditions and exceeds the 20-year reference scenario regarding the two relevant damage mechanisms.

Test designs #3 and #5 clearly fail to

reach equivalence to the reference scenario within a reasonable test time. This is owing to the fact that the temperatures chosen are (too) low (30–45°C) in comparison to the real module temperatures achieved in the field during solar irradiation. For test design #2, whether or not an equivalence to 20 years of outdoor exposure can be reached depends on the chosen time span; for example, 160 hours is too short a time span for correct comparison.

All test designs (including the DLG test) failed to reach equivalence regarding the ammonia diffusion in EVA, which may be relevant at the front side of embedded cells. This is due to the fairly low activation energy for ammonia diffusion within EVA. As a consequence, after any of the proposed tests, the possible damage mechanisms at the front side of the solar cells will not be distributed locally as was the case after the reference scenario. However, this is not a huge drawback: if damage mechanisms are indeed present, they would still be visible or otherwise discernable through their action near the rims of the cells.

Ammonia ingress times through the back sheet, however, do need to be considered. With respect to inner module components, a time lag of around 40 hours (DLG), 50-90 hours (test designs #2 and #3), or 170 hours (DIN 50916) has to be taken into account (cf. Fig. 3). For test design #5 (DIN 50916) in particular, this is a substantial fraction of the total test time, so a correct evaluation of degradation within the module is additionally impeded. As a consequence, the DIN 50916 test is clearly unsuitable for assessing the ammonia resistance of PV modules. In the DLG test design, sufficient time is given for ammonia to reach inner module components and to correctly assess their ammonia resistance.

Some uncertainties are associated with the reported activation energies, such as measurement errors (as in the

	[NH ₃]	humidity	Temp.	time
1.	DLG test (750ppm)	70%	70°C	1,500 h
2.	6,667ppm	100%	60°C	160 h
3.	1,200ppm	85%	45°C	?
4.	HAALT (50,000ppm)	100%	85°C	84 h
5.	DIN 50916 (7,250ppm)	100%	30°C	672 h

Table 1. Different proposed test designs. For some cyclic tests, only the maximum temperature is reported; for test design #2, see [4,17].

determination of the diffusion coefficients) and the identification of the correct damage mechanisms. Therefore, for any test design, it is safest to choose conditions not too far from the estimated maximum temperature in the field (i.e. $\sim 60^{\circ}$ C [14]) and, for acceleration, slightly higher – this was the reasoning behind choosing a temperature of 70°C for the DLG test design.

A cyclic test (as in the proposed variants #2 and #3) may amplify the degradation due to condensation phenomena and may thus be closer to the realistic conditions. However, even under non-cyclic test conditions, capillary condensation occurs within gaps and cavities of a PV module such that the basic difference in the occurrence of damages due to the condensation phenomena is not assumed to be large for PV modules.

Conclusions

Reactive gases introduce a new challenge for the life testing of PV modules. Ammonia gas is the first in line for consideration due to the prevalence of this gas in a major area of the application of PV modules: the agricultural environment, where ammonia gas evolves in substantial amounts in livestock farming. More and more module manufacturers have been reacting to this trend and have been ensuring that their modules are being qualified with respect to ammonia resistance. The most relevant damage mechanism seems to be polymer degradation which affects encapsulant, back sheets, junction boxes, cable sheathing and adhesives, etc. A number of different test designs have been proposed and applied to modules from different manufacturers, some of which fail to reach equivalence with a 20-year reference scenario.

Interestingly, it turns out that double glass PV modules (e.g. with both frontside and rear-side glass) bring certain advantages in a corrosive gas environment versus modules with a polymer (laminate) back side. Not only is a polymer-based module more susceptible to damage from ammonia, but they tend to be basically 'open' to permeation by volatile substances. This advantage of double glass modules could very well be transferable to other corrosive environments such as volcanic sites or in the vicinity of exhaust pipes of fossil fuel burning sites, including motor highways or railway trails. In the future, the prevailing areas of deployment of PV modules will dictate whether the damage caused by other corrosive gases will need to be taken into the consideration for module lifetime estimation.

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