MEASURING AND MODELLING THE GENERATION OF ACETIC ACID IN AGED ETHYLENE-VINYL ACETATE-BASED ENCAPSULANTS USED IN SOLAR MODULES

Luca Gnocchi[1], Alessandro Virtuani[1], Armelle Vallat-Michel[2], Andrew Fairbrother[1], Heng-Yu Li[3], Christophe Ballif [1, 3]
[1]École Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT),
Photovoltaics and Thin Film Electronics Laboratory, Rue de la Maladière 71b, 2000 Neuchâtel, Switzerland
[2]University of Neuchâtel, Platform of Analytical Chemistry, 2000 Neuchâtel, Switzerland
[3]CSEM, PV-center, Jaquet-Droz 1, 2000 Neuchâtel, Switzerland

ABSTRACT: Acetic acid is produced in solar modules encapsulated with an Ethylene Vinyl Acetate based polymer. This is a major issue for the long-term stability of the module performance (i.e. series resistance increase and fill factor reduction). Quantitative assessment of acetic acid generation is necessary for the development of durability models. This step requires the use of invasive techniques, which ultimately destroy the module. In this work, a facile solution to opening modules for measurement of acid concentration is tested. An ETFE foil is placed in between the front/rear glass. It is then straightforward to separate the polymer encapsulant from the laminated stack and collect the produced acid. Liquid Chromatography coupled with a UV detector is the technique used to quantify the acetic acid concentration. The effect of the ETFE foil with respect to a standard module configuration (using one-cell mini-modules) during damp heat test is also assessed in order to understand the viability of the proposed method. Results show a faster degradation during damp heat test when ETFE is present due to faster water diffusion and condensation inside the module, an observation that forces us to be cautious on the validity of the results for samples that do not contain ETFE Finally, a preliminary acetic acid production simulation is shown and compared with the obtained experimental results.

Keywords: Acetic Acid, EVA, degradation, damp heat, module performance, reliability.

1 INTRODUCTION

Acetic acid (HAc) generation is a relevant issue for the durability of solar modules, which make use of Ethylene Vinyl Acetate (EVA) as an encapsulation material. Currently, EVA is by far the polymer most used by the photovoltaic module industry. Despite the presence of alternatives, EVA is still often the preferred choice due its lower price and its proven track record in the field. HAc is mainly responsible for corrosion of metallic interconnections and the consequent reduction of the fill-factor (FF) of the cells, which may lead to a considerable reduction in performance over time [1]. Understanding how the different climatic factors, such as temperature, humidity and UV radiation impact EVA degradation in the long-term is of crucial importance for developing service lifetime model of PV modules.

An important step is the experimental validation of acid generation and degradation models. Accurate quantification of the acetic acid produced inside the module is not trivial, because access to the polymer requires the use of invasive/destructive methods.

We are developing a facile method to extract HAc from modules after Damp Heat (DH) stress tests, in order to validate such models.

2 EXPERIMENTAL

2.1 Sample design

A double glass configuration is chosen to have a structure in which generated acid cannot readily diffuse out of the module, as is the case for a breathable backsheet. Sample size is 20 x 20 cm, and two types of EVA encapsulant are used, including low (28%) and high (33%) VA content. To easily access to the polymer encapsulant, an ETFE foil is put in between the EVA and the glass super- and substrates as shown in Figure 1a. To understand how the ETFE foil is influencing the results with respect to a standard module stack (e.g. no ETFE in between the polymer and the glass), 1-cell mini modules are also laminated and tested in parallel with both configurations (i.e. with and without ETFE foil). The cells are standard Al-Back Surface Field (BSF).

2.2 Aging conditions

All samples are tested under Damp Heat stress conditions (T=85°C and RH=85%). The usual test duration (e.g. 1000h) has been extended up to 3000h to enhance the acetic acid production. Samples manufactured simultaneously and with the same materials, for which we assume a similar behaviour, are exposed in DH for intervals of 1000 hours, before they are separated to extract the EVA used in the analysis.

2.3 Acetic acid extraction

The module stack is mechanically separated to isolate the EVA film. The use of ETFE greatly reduces adhesion between the glass and encapsulant, allowing for facile separation. During and after this stage, water is used to rinse all surfaces (glass, ETFE, EVA) and collect the generated acetic acid. The water is then collected and analysed in the chromatographer.

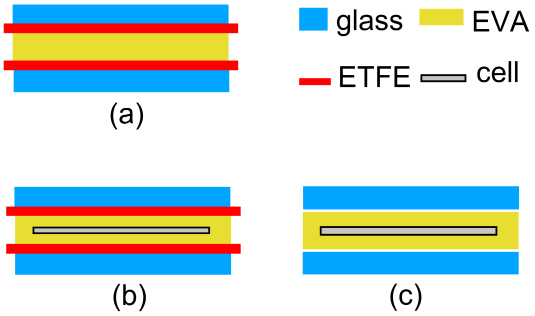

Figure 1: cross-sectional sketch of the sample structures used during the experiments: Glass/ETFE/EVA/ETFE/Glass (a) used to measure the acetic acid production; 1 cell mini-module structure Glass/ETFE/EVA/cell/EVA/ETFE/Glass (b) used to understand the impact of ETFE w.r.t a standard 1 cell mini-module configuration: Glass/ EVA/cell/EVA/Glass (c)

2.4 Chromatography

To quantify the acetic acid concentration High Performance Liquid Chromatography (HP-LC) is used. The column used for the separation is a PrevailTM Organic Acid (Grace Davison Discovery Sciences, Deerfield, IL). 50 mM phosphate buffer at pH 2.5 is used as the solvent. The temperature of the column is set at 40°C. The injected volume is 10 µL. The acetic acid is detected by UV radiation at 210nm. Measurements are done after 600, 1000, 2000 and 3000 hours of DH duration.

2.5 Module performance

Module performance is assessed by means of current-voltage (I-V) measurements, electroluminescence (EL) images and visual inspection

2.6 FEM model

Simulations of acetic acid generation are carried out using COMSOL Multiphysics® 5.3 and its "Transport of diluted species" module. The modelling geometry consists of a 2D structure representing a vertical cut through the glass/EVA/glass structure as shown in Figure 1a. In this configuration, only the borders are set as an open boundary with a constant concentration set to zero. A source term is also included in the solute conservation equation. The source term initial value at 27°C and Arrhenius dependency are taken from literature [2]. The acetic acid diffusion coefficient in EVA along with its Arrhenius activation energy values are also taken from the literature [3].

Table I: EVA properties used for the FEM model

Ref.	Property	Value (ref. T)	Activation. En. [kJ/mol]
[2]	Source term [ng/min/g]	0.00331 (27ºC)	90
[3]	Diff. coeff. [m^2/s]	$1 \cdot 10^{-11}$ (50ºC)	35

3 RESULTS

3.1 Acetic acid production

Figure 2 shows the acetic acid concentration measured for the two different EVA samples after exposure to DH for different intervals. Measured values after 3000 hours of DH fall in the range 0.5-0.6 mg/g, values consistent with previously reported figures [4, 5, 6]. The curves show the same behavior with a plateau around 2000 hours of aging. This result is in agreement with what is shown by Masuda et. al [6] when using non-permeable backsheets, which, in regards to trapping acetic acid and limiting water diffusion, is comparable to the double glass configuration adopted in this work.

The slight acetic acid concentration reduction measured at 3000 hours can be related to some experimental errors (e.g. longer delayed time before the analysis).

As expected, a higher concentration of acid is produced in the EVA that has the higher VA content. This result is useful because it confirms the accuracy of the chromatography type used to analyse samples.

3.2 Module performance

The importance of a precise HAc concentration measurement is also highlighted in Figure 3, which shows the maximum power (Pmax) and the fill-factor (FF) losses during DH of 1-cell mini-modules encapsulated with the two EVA formulations.

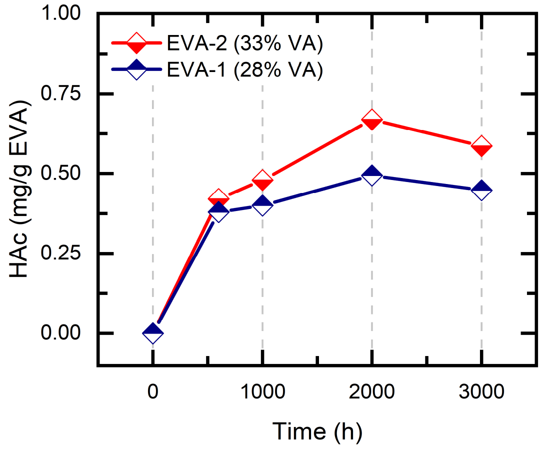

Figure 2: acetic acid concentrations (HAc) measured for the samples with the two different EVAs: 28% (blue line) and 33% (red line) VA content after exposure to DH for different intervals.

Modules encapsulated with higher VA content EVA exhibit major degradation. The most affected parameter is the FF as a consequence of HAc produced in the module. After 3000 hours of aging, a 10% difference in FF loss is reached between the two tested modules. Short circuit current (Isc) and open circuit voltage (Voc) stay stable during the duration of the experiment (curves not shown).

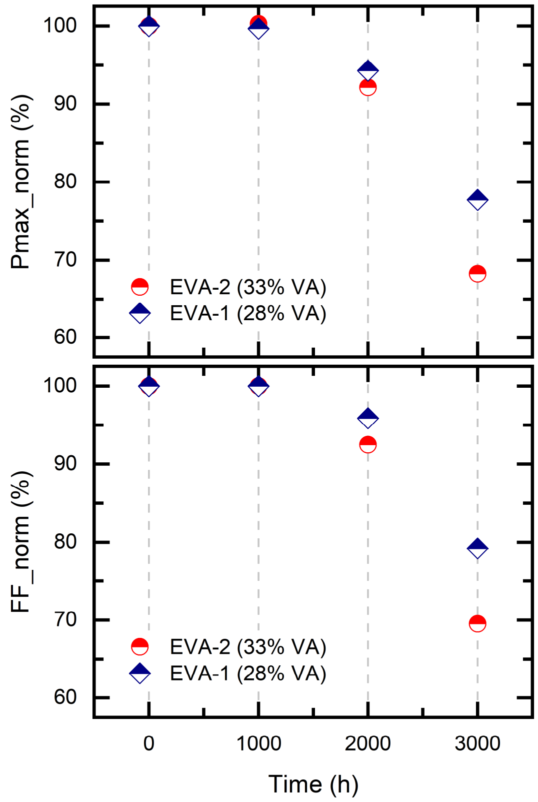

Figure 3: performance of the 1cell mini-module manufactured with the two different EVA formulations as a function of the time spent in DH during DH test: Pmax (above) and FF (bottom) comparison between EVA with 28% (blue squares) and 33% (red circles)

VA content.

The influence of the addition of ETFE foils in between front (and rear) glass and the polymer is also studied. Figure 4 compares two 1-cell mini-modules encapsulated with the same EVA type (e.g. 28% VA). Blue squares are related to a standard double glass structure, whereas the light-blue circles correspond to the stack on which the ETFE is added.

The different degradation rate is already detectable after 1000 hours of DH. In addition to a faster FF loss and series resistance increase (curves not shown), the Isc value shows a gradual reduction for the module encapsulated with the ETFE foil.

The unexpected observation that mini-modules with the ETFE foil degrade more is not a good news.

It could be a limit to the adoption of the method and to the "transferability" of the results to real modules (samples not containing ETFE).

The results show a faster degradation in performance of the modules during damp heat test when ETFE is present. This is likely due to a faster diffusion of the water from the edges and to a consecutive condensation inside the module, as visual inspection and EL images suggest, in Figure 5. The water that condenses inside the module accelerates the corrosion and decreases the transmittance by creating a new interface. This can explain the gradual current loss appearing in modules tested with the ETFE foil.

This observation forces us to be cautious on the validity of the method and on the possibility to use the results as a proxy for the samples that do not contain ETFE, for which a possible reduced water content would likely occur. The method described here requires hence a more detailed validation.

3.3 FEM model

The comparison of the model and experimental results is shown if Figure 6. In the model only the thermal stress is present. Relative humidity is an important factor during the damp heat experiment, so this leads to an under estimation of the HAc production inside the module.

This lack should not affect starting values, when the humidity still has to diffuse inside the sample. However, the comparison already after 600 hours shows remarkable differences. This discrepancy can be attributed to the different EVA properties, as the one used in the model are taken from the literature. Activation energies and/or source term can vary depending on the adopted polymer formulation. Another explanation can be accorded to the faster water diffusion due to the presence of the ETFE layer inside the samples. It is probable that, with no adhesion between the G/ETFE interfaces, the humidity is already present overall the front surface. As reported in Figure 5, finger failures are already detectable after 1000 hours of DH.

However, the order of magnitude is comparable with the measured values. To improve the accuracy of the simulations hydrolytic stresses will be introduced, in addition to using more accurate material property values (i.e. diffusion coefficient and HAc source term), rather than literature values.

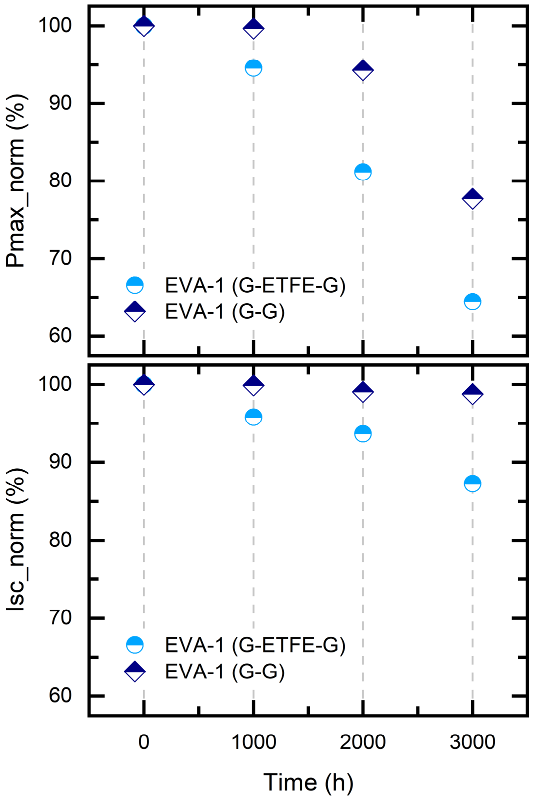

Figure 4: 1 cell mini-modules performance during DH test: Pmax (above) and Isc (bottom) behavior; comparison between Glass/ETFE/EVA/cell/EVA/ETFE/Glass (light blue circles) and standard Glass/EVA/cell/EVA/Glass (blue squares) configuration.

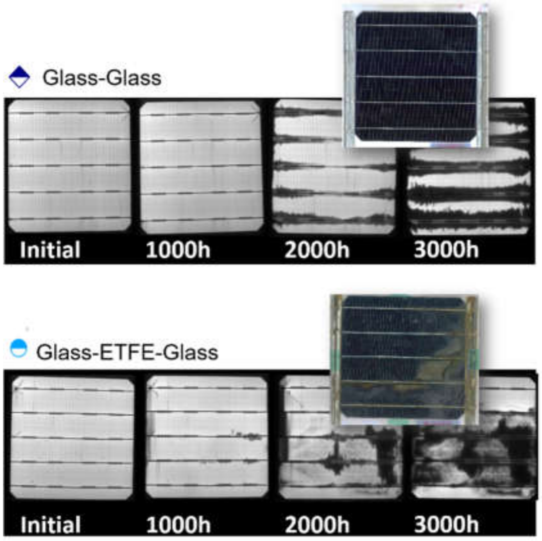

Figure 5: EL images before DH and after 1000, 2000 and 3000 hours of DH test, along with a visual image after 3000 hours of DH. Above: standard G-G structure; bottom: Glass/ETFE/EVA/cell/EVA/ETFE/Glass stack.

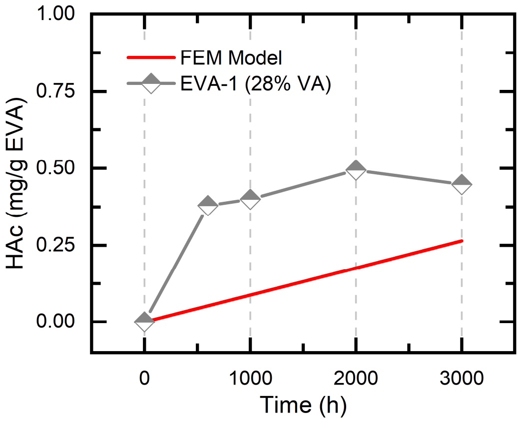

Fig.6: HAc production comparison during DH test: experimental values (grey curve) and FEM model (red line).

4 CONCLUSIONS

With the insertion of an ETFE foil between the glass and the encapsulant in glass/EVA/glass samples (i.e. glass/ETFE/EVA/ETFE/glass) we are able to easily open –up the samples and get access to the polymer encapsulant for analysis.

For this study two different formulations of EVA with low (28%) and high (33%) VA content are used.

The analysis is performed on samples manufactured simultaneously after the exposure of the samples in damp-heat for intervals of 1000 hours (up to 3000 hours) using Liquid Chromatography coupled with a UV detector. LC-UV is able to quantify the content of the acetic acid generated in the encapsulant due to water ingress from the edges in the samples at high temperatures, and that the quantity of HAc generated clearly depends on the chemical formulation of the EVA.

As expected, a higher concentration of acid is produced in the EVA that has the higher VA content.

In addition, a preliminary simulation of acetic acid production in the samples using a FEM has been performed and compared with the results obtained experimentally. Hydrolytic (and UV) stresses will need to be added in the model in order to improve its accuracy.

Additionally, one-cell mini-modules with the same structures (i.e. glass/EVA/cell/EVA/glass and glass/ETFE/EVA/cell/EVA/ETFE/glass) are prepared and subjected in parallel to DH aging in order to understand the viability of the proposed method.

The results show a faster degradation in performance of the modules during damp heat test when ETFE is present, due to a faster water diffusion and condensation inside the module. This observation forces us to be cautious on the validity of the method and on the possibility to use the results as a proxy for the samples that do not contain ETFE. The method described here requires hence a more detailed validation.

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