

X-Ray Study on Damp-Heat Induced Cell Degradation (DHID)

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ABSTRACT: Ethylene vinyl-acetate (EVA) is a commonly used encapsulation material in the PV industry. Although EVA degrades under various climatic conditions forming acetic acid, its relatively low price and missing experience with alternative materials makes it the predominant choice for encapsulation material.

Chemical reactions, which occur during extended damp-heat (DH) conditions (90 °C/85 % r.h.) between the degradation by-products of EVA and other involved components like e.g. the metallic compounds or the glass of the metallisation, may result in metallisation corrosion and in isolated areas of the cell, visible in the electroluminescence images. To evaluate the actually affected components and accelerating conditions to this phenomenon, several parameters of the laminate design, such as number of bus bars (two or three) or the distance from the bus bar to the glass and the back sheet material (TPT, TPAT, PA) were varied. The produced laminates were then exposed under extended DH conditions to reveal the accelerating factors for the metallisation corrosion. In addition to this preliminary work, the herewith presented study of X-ray investigations (X-ray diffraction and EDX spectroscopy studies) were carried out on the metallisation and the degradation products.

Keywords: X-ray diffraction, metallization, EVA, acetic acid, corrosion, photovoltaics

1 INTRODUCTION

The reliability and degradation mechanisms of PV modules comprising a front glass cover and a polymeric back sheet have been subject to extensive research [1]. Since more than two decades, EVA is used as an encapsulant material. EVA may degrade under acetic acid formation, thus affecting the reliability of the metallic compounds in the module, especially the cell metallisation. Acetic acid is assumed to be an acceleration factor or even cause for classic corrosion. Standard front side metallisation uses lead-glass for an effective contact formation between the screen printed silver grid and the silicon cell. The silver paste for the screen printing consists of silver, glass, cellulose resins, organic solvents and inorganic additives [2, 3]. Within the firing process a silver-lead-phase is obtained in the glass penetrating the AR-coating down to the silicon cell.

induced cell degradation [1] revealed the crystal growth of acicular crystals on the top and bottom of the degraded grid fingers. By means of energy dispersive X-ray spectroscopy (EDX) measurements of these acicular crystals the elements lead, carbon and oxygen could be assigned as main parts of the composition. This result led to the assumption that the degradation of the metallisation was connected to the formation of lead acetate, $Pb(CH_3COO)_2$.

The aim of the herein presented X-ray study, a combined X-ray diffraction and EDX spectroscopy study was to identify the chemical composition of the needles or other degradation products in order to reveal the reaction mechanism of the damp-heat induced cell degradation.

2 EXPERIMENTAL

The damp-heat induced cell degradation was studied by means of EDX and X-ray investigations. X-ray diffraction measurements enable total phase analysis of the investigated specimens. In the herein presented work the degraded laminates (glass-EVA-cell-EVA-back sheet (here: TPT) configuration) were opened from the rear side (polymer back sheet) through the EVA encapsulant to obtain cell fragments with the degraded metallisation. Two samples were made from the received cell fragments.

The first sample was prepared in order to receive the degraded metallisation and the assumed degradation product, lead acetate, by mechanical peeling of the metallisation from the cell. For the X-ray diffraction measurements a milling of the solid sample was required.

A second approach to elucidate the existence of lead acetate to the degraded metallisation was the use of the excellent water solubility of lead acetate. The cell fragments were poured in water and stored for several weeks under constant stirring. After the suspension was filtered and dried, the obtained powder was milled and diluted with glass-powder (sample #2). The additional dilution with glass-powder was utilized to enlarge the amount of powder for the X-ray diffraction measurements. The measurements themselves were accomplished by the help of a Bruker-D8 Advance

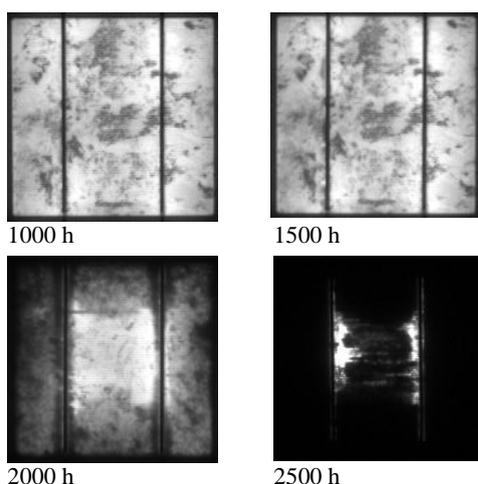


Figure 1: Electroluminescence images of laminates after different time steps of extended DH-testing (90 °C/85 % r.H.).

The electroluminescence images, presented in figure 1, show the growing inactive areas of a cell during the exposition to extended DH conditions (90°C/85r.h.) for up to 2500 h. The preliminary work on the damp-heat

diffractometer, equipped with a 1D-Lynxeye™ detector and a silicon sample holder using Bragg-Brentano geometry. Cu-K α radiation was used with a 0.02° step size and 60s/step. For the EDX spectroscopy measurements, the powders of sample #1 and #2 were fixed by means of a graphite tape on the sample holders. The EDX measurements were carried out at an Environmental Scanning Electron Microscope ESEM (FEI Quanta 400) with integrated EDX spectroscopy (EDAX Genesis). Pictures were taken at an accelerated voltage of 25 kV.

3 RESULTS

The results of the X-ray diffraction and EDX spectroscopy measurements of the grey powder of sample #1 and the white powder of sample #2 are shown in section 3.1 and 3.2, respectively.

3.1 X-RAY DIFFRACTION

Figure 2 shows the X-ray powder diffraction measurements of sample #1. Silicon, aluminum and silver phases may be identified as phases of the powder, which form the main parts of the cell and the metallisation. Because the preparation was carried out from the rear side of the laminates, aluminum, which is used for back side metallisation, is contained. The silicon phase may be detected because of the mechanical peeling of the grid with a tweezers. Other phases are either not present or the intensity/concentration not significant enough in comparison to the silicon, aluminum and silver phases.

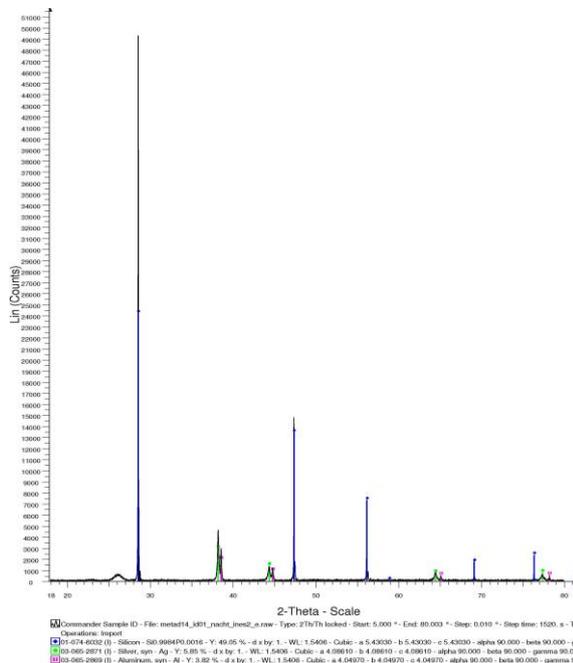


Figure 2: X-ray diffraction data of sample #1, with indexed Si-, Al- and Ag-phases.

The second powder diffraction measurement, shown in figure 3, shows a highly amorphous phase, caused through the dilution of sample #2 with glass-powder. In addition to the amorphous phase, silver may be identified as a single phase in the powder. A lead or lead acetate phase could not be indexed by the X-ray diffraction data.

The presence of silver, however, was not expected due to the fact that the powder was water soluble. Silver was either obtained in the powder as water soluble silver salt or due to a faulty grain size of the filter. The all-white powder after the water evaporation and the fact that dark particles were only seen after the sample has been exposed to daylight promotes the first assumption.

Since silver acetate is partly soluble in water and very sensitive to light, it is possible that silver acetate, Ag(CH₃COO), was present in the sample. The formation temperature of Ag(CH₃COO) from acetic acid and silver-ions, which are always present in an aqueous equilibrium state, is found to be above 40°C. Within the water evaporation this temperature was significantly exceeded.

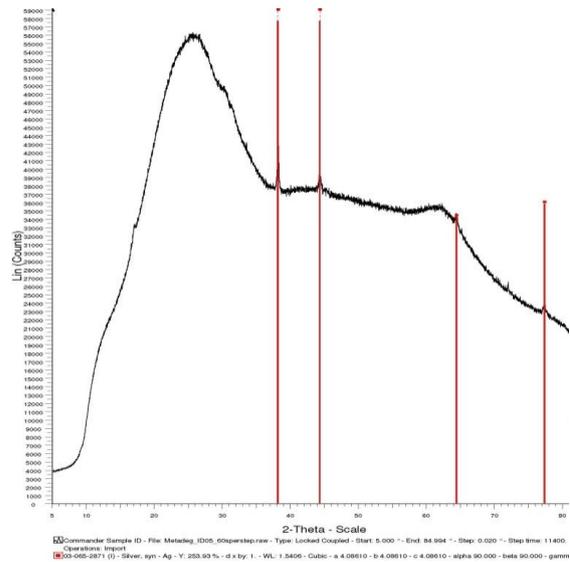


Figure 3: X-ray diffraction data of sample #2, with indexed Ag-phase.

3.2 EDX SPECTROSCOPY

The EDX spectroscopy measurements of sample #2 were carried out after the X-ray diffraction measurements to validate the negotiation of the presence of lead acetate. Figure 4 shows the ESEM image of some particles of sample #2 detected with a back scattering electron (BSE) detector, which shows a Z (atomic number)-mapping, an element-specific contrast, of the sample. As seen in figure 4, there is only one bright particle in the measured range, which was identified as silver by means of EDX measurements.

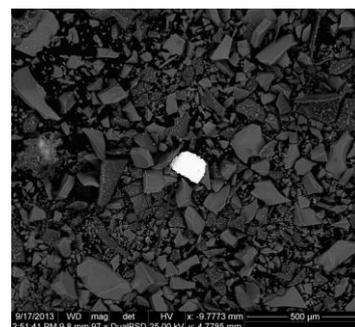


Figure 4: ESEM image (BSE detector – Z-contrast) of some particles of sample #2.

This indicates that silver is only a by-product and the main phase of the X-ray diffraction pattern of sample #2 was superimposed by the amorphous glass phase. Figure 6 shows a more detailed, selected region of sample #2, taken with ESEM and BSE-detector.

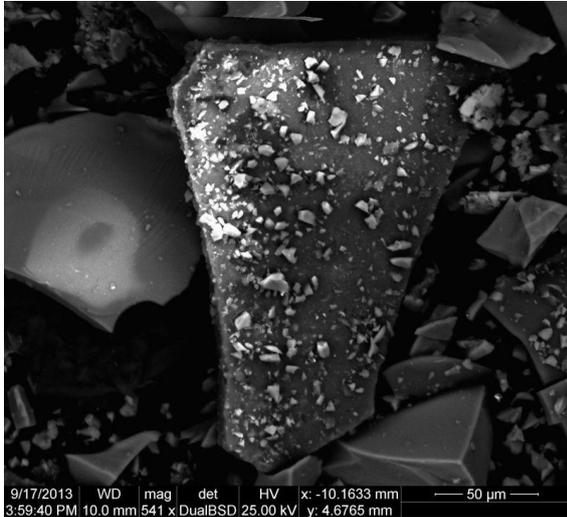


Figure 6: ESEM image (Back Scattering Electron BSE detector) of some selected particles of sample #2.

An element mapping by EDX measurements of these particles revealed that the particles either consist of silicon (blue spots in figure 7) and oxygen (red spots), due to the dilution of glass-powder, or they consist of lead (yellow spots), carbon (red spots) and oxygen (red spots).

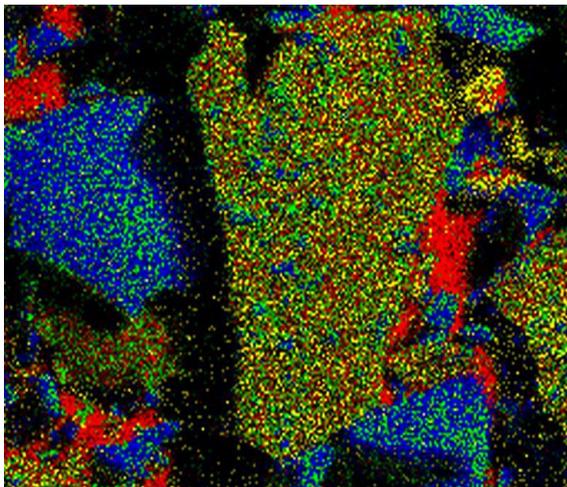


Figure 7: EDX element mapping of some selected particles of sample #2 (blue spots: silicon/ green spots: oxygen/ reds spots: carbon/ yellow spots: lead).

The small particles, which are distributed over the largest particle, shown in figure 6, may be identified as glass (see fig. 7). The element mapping also shows the evermore coexistence of lead with carbon and oxygen, indicating again the presence of lead acetate.

4 CONCLUSION

The combined X-ray diffraction and EDX spectroscopy investigations of sample #1 showed the existence of silver (Ag), aluminum (Al), sodium (Na), silicon (Si) and lead (Pb) in the mechanical peeled sample #1 of degraded grid. The lead phase could not be identified with the help of X-ray diffraction measurements, either because of the low concentration of the phase or because of the high intensity of the Si pattern.

The measurements of the water extracted substance (sample #2) identified a carbon and oxygen containing lead phase, the additional added glass-powder and silver. The Z-contrast ESEM images showed only a very low number of silver particles, indicating that silver may be considered as an impurity.

The fact that most lead salts show a poor water solubility, except of lead acetate, $Pb(CH_3COO)_2$, supports the conclusion of the presence of lead acetate in the degraded metallisation of the damp-heat induced cell degradation. The results showed that combined X-ray diffraction and EDX spectroscopy measurements represent a good choice for the study of the damp-heat induced cell degradation.

5 LITERATURE

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