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INVESTIGATING THE DEGRADATION OF FRONT AND REAR SIDES OF C-SI PV CELLS EXPOSED TO ACETIC ACID

Nikoleta Kyranaki*, Jiang Zhu1, Ralph Gottschalg2, Thomas R. Betts1
Centre for Renewable Energy Systems Technology (CREST), Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, LE11 3TU, United Kingdom
Fraunhofer Center for Silicon Photovoltaics CSP, Halle, Germany
*N.Kyranaki@lboro.ac.uk, +44 (0)1509 227161

ABSTRACT: The goal of this paper is to investigate the reactions responsible for the degradation of the front and rear side of c-Si solar cells that are immersed in acetic acid solutions. The types of degradation are characterised by electrical, optical and chemical methods. The identified degradation modes are compared to those observed in PV cells undergoing damp-heat aging. The degradation of the power output of a PV cell exposed under damp-heat conditions typically is observed after 3000-5000 hours of exposure. The purpose of this work is to research if acetic acid immersion of PV cells can result in the same types of degradation observed for damp-heat aging and how these degradation modes affect their power output. It is observed that acetic acid immersion and damp-heat exposure show a similar mechanism of degradation. This degradation is identified to occur because of reaction of acetic acid with lead, tin and aluminium. Lead and tin migration causes separation of the ribbons and the silver contacts from the cells. Aluminium corrodes severely because of presence of moisture, causing a series resistance increase of the cells.

Keywords: Back contact, degradation, metallization

1 INTRODUCTION

PV modules that are encapsulated with ethylene-vinyl acetate (EVA), typically show degradation of their power output after Damp-Heat (DH) exposure for 3000-5000 hrs [1]. The most relevant degradation path is that acetic acid is produced because of moisture penetration and high temperature and attacks the metallization, the ribbons and the aluminium (Al) back contact of the PV cell [2, 3]. The exact degradation mechanisms and the impact of the different mechanisms on the power output of a solar cell, are not fully understood yet. The purpose of this work is the simulation of the effects of DH aging by acetic acid immersion, the identification of the responsible aging mechanisms and the separation of the impact of corrosion on the different components of a PV cell.

2 EXPERIMENTAL SETUP

Commercially available c-Si PV cells soldered with Pb-Sn-Cu ribbons are immersed into acetic acid solutions of different concentrations at room temperature. The different concentrations are 30%, 10% and 0.3% v/v. The two first concentrations are used for accelerating aging and better understanding of the reactions. The third concentration is that detected in PV modules aged under damp-heat conditions [4]. The acidity and the temperature of the solution are monitored with a pH meter and kept at pH 1.9+/0.2, 2.3+/0.2 and 3.4+/0.2 respectively. The PV cells are soldered manually using a commercial standard flux, and a standard 2-mm-wide Pb-Sn-Cu ribbon. For better mechanical stability and for the ability to age only one side of the cell, the cells are half encapsulated in a glass-EVA-cell structure (Fig. 1). For the investigation of corrosion of the back contact of the cells, the laminate structure is the same as for the front side aging but the front side of the cell faces the encapsulant and the back side is exposed (Fig. 2).

3 CHARACTERISATION METHODS

The process of the experiment and the characterisation methods is presented on the flowchart (Figure 3) below:

3.1 I-V curve measurements
The samples were removed from the acetic acid solution every 2 days for Light I-V curve measurements at STC by Pasan IIIb solar (flash) simulator.
3.2 Electroluminescence
Electroluminescence (EL) images are captured every 2 days for the observation of the impact of the acetic acid on the contacts and the ribbons (increased series resistance, shunting).

3.3 Material/chemical analysis (SEM-EDS analysis, optical microscopy)
Optical microscopy is used as a non-destructive method for the observation of material changes during the experiment, due to acetic acid exposure. SEM-EDS analysis is used as the final destructive characterisation method for the identification of the migration of the different elements, due to material reaction with acetic acid.

4 THEORY OF POSSIBLE REACTIONS
In this work the reactions that are mainly reported in literature between acetic acid and the different components of a PV cell, will be verified.

4.1 Silver front contact and metallisation corrosion
For the manufacturing of the solar cell front contacts, normally a silver paste is applied by screen printing, which includes glass frits containing lead oxide. Acetic acid attacks the lead oxide, according to the following reaction [5]:

\[ \text{PbO} + 2\text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{O}. \]  

Because of this reaction, the silver contact is separated from the cell.

4.2 Back contact corrosion
During the acetic acid immersion of the cells, most likely the Al from the Al-back contact reacts with acetic acid. The reaction is presented below [6]:

\[ \text{Al} + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3/2\text{H}_2 \uparrow \]  

This process is responsible for reducing electrical conductivity and an increase of the series resistance [7].

4.3 Ribbon corrosion
For the construction of the ribbons of a PV cell, normally alloys of tin (Sn) and lead (Pb) are used as a solder. Acetic acid attacks the solder, and the reaction is:

\[ \text{Sn} + 2\text{H}^+ \rightarrow \text{Sn}^{2+} + 2\text{H}_2 \uparrow \]  
\[ \text{Pb} + 2\text{H}^+ \rightarrow \text{Pb}^{2+} + 2\text{H}_2 \uparrow \]  

Because of the solder leaching, the silver contact and the ribbon are separated [6]

5 RESULTS
5.1 Light I-V curves
In Figure 4 the degradation of the performance parameters of the cells immersed in different concentrations of acetic acid solution is presented. For 30% concentration the degradation of short circuit current (Isc), fill factor (FF) and maximum power (Pmax) (-8%) are bigger than those for 10% concentration (-2%). The increase of series resistance is most likely the reason for the FF degradation, as change of the slope of the I-V curve close to open circuit voltage ( Voc) is observed.

Figure 5 illustrates the performance parameters for the cells with the Al-back side exposed to the acetic acid. The cells immersed in higher concentrations (30% and 10% v/v) show a slower degradation than the cells immersed in 0.3% concentration. The power output degradation is totally driven by FF reduction, and the Voc remains almost constant. The reduction of the Pmax is around -25% for all of the samples, but for the higher concentrations, this level of reduction is reached after 900 hrs, in contrast to the samples immersed in 0.3% concentration, which reach this reduction in only 200 hrs of immersion. This likely happens because the reaction of Al with acetic acid produces aluminium acetate which inhibits further reaction. The Al-back contact corrosion seems to be more serious than the ribbon and silver contact corrosion because the degradation of the Al-back contact causes a bigger reduction on the power output of a PV cell (-25%) than the front side degradation (-8% worst case).
5.2 Electroluminescence

Figures 6 a and b represent the EL images of an unaged and an aged cell. The bright areas along the busbars of the immersed into acetic acid PV cell, are an indication of series resistance increase.

![Image](Figure 6: Images of a) an unaged and b) an aged solar cell.)

5.3 Material analysis

Figures 7 a and b show the optical microscopy images of the metallization and the ribbon of an unaged and an aged in 30% concentration of acetic acid solution cell. Brown patterns on the ribbon and the metallization are visible which are identified by EDS analysis as copper (Cu) from the ribbons (Figure 10). The colour of the cell appears to be brighter blue for the aged cell. This is an indication of corrosion of the anti-reflection coating. The optical microscopy image of the cell immersed in 10% concentration of acetic acid solution (Figure 8 a and b) shows some white patterns on the metallization. On the EDS analysis of the samples (Figure 11) the white patterns are recognized that are caused because of Sn and Pb migration from the ribbons or the contacts and the metallization. According to the measurement of the ribbon composition, Pb is observed to dissolve more (Figure 12). This phenomenon can be explained, because for 30% concentration of acetic acid, the dissolution of Sn and Pb is very fast, and the core Cu of the ribbons is more exposed into acetic acid, so, it also starts to dissolve. For 10% concentration, the reaction is slower and the most observable migration is this of Sn and Pb.

Figures 9 a and b illustrate the optical microscopy images of an unaged and an aged back contact of a silicon solar cell. The leaching of the Al is visible, as some white and brown patterns as well. The Al leaching can be confirmed also by the EDS analysis of the sample (Figure 13) and the white and brown patterns are identified as Sn/Pb and Cu, respectively.

![Image](Figure 7: Optical microscopy images of the metallization and the ribbon of a) an unaged and b) an aged cell in 30% concentration of acetic acid solution.)

![Image](Figure 8: Optical microscopy images of the metallization and the ribbon of a) an unaged and b) an aged cell in 10% concentration of acetic acid solution.)

![Image](Figure 9: Optical microscopy images of a) an unaged and b) an aged back contact of a silicon solar cell.)

![Image](Figure 10: SEM-EDS analysis of the silver contact and the metallization of an aged cell in 30% concentration of acetic acid solution.)

![Image](Figure 11: SEM-EDS analysis of the silver contact and the metallization of an aged cell in 10% concentration of acetic acid solution.)

![Image](Figure 12: Material composition of a) an unaged and b) an aged ribbon.)

![Image](Figure 13: SEM-EDS analysis of an aged back contact of a silicon solar cell.)
6 COMPARISON WITH DAMP-HEAT

6.1 Light I-V curves

In Figure 14 the degradation of a 6-cell mini-module aged in DH conditions (85°C/85%RH), is visualized. By combining the impact of front side acetic acid immersion (Isc and FF reduction) and of Al-back contact acetic acid immersion (FF reduction), a similar degradation pattern to that caused by DH aging is observed. The degradation is more accelerated and sudden for high concentrations of acetic acid. The cells immersed in 0.3% concentration, for duration of immersion of 2000 hrs, do not show any degradation. This behaviour is similar to that of the modules aged under DH conditions, as, for 2000 hrs of DH aging, degradation is also not observed.

![Figure 14: Degradation of the performance parameters of a 6-cell mini-module aged in DH conditions (85°C/85%RH).](image)

6.2 EDS analysis

From the EDS analysis of a ribbon of a cell immersed in acetic acid solution (Figure 15) and a ribbon of a mini-module aged in DH conditions (Figure 16) it is clear that the material reactions are similar to acetic acid immersion, as the alloy of Sn and Pb is visibly corroded, and the Cu is detectable, because of the dissolution of Sn and Pb.

![Figure 15: SEM-EDS analysis of a ribbon of a cell immersed in acetic acid solution.](image)

![Figure 16: SEM-EDS analysis of a ribbon of a mini-module aged in DH conditions.](image)

7 CONCLUSIONS

For front side immersion in 30% concentration of acetic acid the degradation of Pmax is bigger and driven by FF degradation. The Isc degradation is smaller and probably caused by the antireflection coating degradation. For 10% the degradation of the performance parameters is smaller and more sudden. The degradation for the cells immersed in 0.3% concentration of acetic acid is negligible. When the Al-back contact is immersed into acetic acid of high concentration does not corrode severely, because of the aluminum acetate (inhibitive complex) that is produced by the reaction of Al with acetic acid. On the contrary, when the acetic acid concentration is low, water is highly corroding for the Al. From these findings we can conclude that the most serious power output reduction occurs because of moisture corrosion of the Al-back contact.

From the material analysis it can be concluded that for the highest concentration of acetic acid, copper has also migrated from the ribbons towards the cell, as the dissolution of the alloy of Sn and Pb is faster. Pb is observed to dissolve even more. For a lower concentration, the Sn and the Pb are mostly detected. In addition, the leaching of the Al from the Al-back contact is visible.

From the comparison of acetic acid immersion of the cells with damp heat aging of modules, we can conclude that acetic acid immersion and DH aging show a similar degradation pattern of the electrical parameters of the modules/cells, FF reduction mainly due to Al-back contact degradation (smaller FF reduction for the front side immersion), and Isc reduction due to front side degradation (no Isc reduction is observed for the Al-back side immersion). In addition, from the EDS analysis, it is observed that the mechanism responsible for the degradation that occurs under DH condition is similar to the mechanism reproduced by acetic acid immersion, as Sn and Pb migration from the ribbons are observed for both acetic acid immersion and DH aging.

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9 REFERENCES