AE Studies on the Durability of Flexible Dye-Sensitized Solar Cells

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Abstract
Tensile test of transparent conductive oxide (TCO) deposited on polyethylene naphthalate (PEN) film (TCO + PEN film, Peccel Technologies, PFCF), which is used for dye-sensitized solar cells (DSCs), was carried out in this study. The result of tensile test showed that many AE signals were detected in TCO + PEN film, while few AE signals in PEN film (TCO was removed by dilute hydrochloric acid). Electrical resistance of TCO was also measured during tensile test. AE event rate began to increase at the strain of 0.63%, and electrical resistance increased rapidly at the strain of 0.68%. These results suggested that critical damage in TCO was detected by AE monitoring more sensitively than electrical resistance. In-situ observation of specimen during tensile test demonstrated that cracks transverse to the loading direction in the TCO were initiated at the strain of ~0.67%, and then saturated at the strain of 9.63%. It was emphasized that AE signals correspond to the cracks in TCO. Damage in TCO under mechanical strain was successfully monitored by AE technique. Consequently, it was suggested that AE technique will be a powerful technique for detecting degradation of DSCs.

Keywords: Dye-Sensitized Solar Cells, Transparent Conductive Oxide Film, Microdamage Accumulation, AE Monitoring

1. Introduction

Solar cells have been developed for expanding the utilization of sustainable energy. Especially, dye-sensitized solar cells (DSCs) are expected as a new generation solar cells because of its low production cost. Furthermore, flexible substrates impart flexibility to DSCs, which become attractive in industrial application. However, it is well known that they have a disadvantage of short lifetime under the condition with mechanical loading. It is then necessary to understand both the damage mechanism and the influence of damages on the degradation in electrical performance of DSCs. Therefore, the technique for damage monitoring is a key technology for the durability of DSCs.

However, it is difficult to identify the mode of microdamage in the whole DSC module, because various damages nucleate sequentially and simultaneously. It is, therefore, required to understand the damage mechanisms of individual components of DSCs such as the transparent electrode, i.e. the transparent conductive oxide (TCO) deposited on the polyethylene naphthalate (PEN) films.

Several investigations were reported on the damage accumulation process in TCO + PEN films [1-3]. However, the time and critical strain of damage initiation in TCO were not identified, although they yielded indispensable implications for the reliability of DSCs. On the other hand, the microdamages in various materials could be correlated to detected AE signals by the authors [4]. In particular, mechanical damage accumulation in a-Si:H solar cells under tensile strain was monitored by AE technique [5].

The final goal of this study is to clarify the damage mechanism in DSCs and the influence of damage on the degradation in electrical performance of DSCs. As the first step, the purposes
of the present paper are to establish the monitoring technique of mechanical damage in TCO and to understand the damage accumulation process of TCO + PEN films under tensile load using AE technique. The tensile tests of TCO + PEN films were carried out. Especially, the relationship between AE behavior and damage accumulation in TCO + PEN films is discussed in the present paper.

2. Specimen preparation and experimental procedure

2.1 Specimen

In the present paper, TCO (= tin-doped indium oxide, ITO) deposited on PEN films (Peccel Technologies, PFCF) were used as a specimen. Appearance and geometry of TCO + PEN film, which is used as a transparent electrode in the DSC module, are shown in Figure 1. As shown in Figure 1 (b), the thickness of TCO layer is 300 nm, which is thicker than those usually used for touchscreens etc. so that the film has lower resistivity.

The coupon specimens with dimensions of 10×130×0.2 mm were cut from the TCO + PEN film. This type of specimen was named “Specimen A”. In order to discriminate AE signals from TCO and PEN films, PEN film specimens (TCO was removed by 17.5% hydrochloric acid) were also prepared and termed “Specimen B”.

2.2 Experimental procedure

Experimental apparatus is illustrated in Figure 2. Tensile tests were carried out at room temperature in air. Tensile load was applied to the specimen using a universal testing machine (Shimadzu, AG-1000E) along longitudinal direction under constant crosshead speed of 0.1 mm/min. Apparent strain was calculated from the crosshead displacement. During the test, AE signals were monitored by three broadband AE sensors (NF, AE-900M). One sensor was attached at the center of the gauge length (60mm). The others were attached close to the holding grips and used as guard sensors, by which mechanical noises from testing apparatus were detected earlier than the central sensor, thereby they could be discriminated from the AE signals due to microdamages. The AE signals were amplified by 40 dB and the threshold level was set to 50 µV at the input terminal of the sensors, and a band pass filter was selected at a
The AE signals were recorded and processed by an AE analyzer (Vallen Systeme, AMSY-5).

Wave propagation characteristics in the specimen were examined prior to tensile tests using similar system as shown in Figure 2. Two broadband sensors (NF, AE-900M) were used as a pulsar and a receiver. The distance between two sensors was 0, 6, 12 mm to measure the attenuation of AE waves in the specimen. Furthermore, mechanical load was applied to the specimen for characterizing the effect of strain. Swept sine wave, described in Figure 3, was used as an input signal. It has a frequency range up to ~2 MHz for the duration of 100 μs.

![Figure 2. Tensile test and AE measurement system](image)

![Figure 3. Waveform and wavelet transform of swept sine signal](image)
To investigate the effect of damages on the electrical performance of TCO, electrical resistance was measured by a two-terminal method. Electrical leads were attached on the specimen surface using conductive tapes. A distance between two conductive tapes was 40 mm. An electrical circuit consisting of a bridge box and a strain amplifier, which is usually used with strain gauges for the strain measurement, was utilized for measuring the electrical resistance. Electrical resistance was also recorded by the AE analyzer.

3. Results and discussions

3.1 Wave propagation behavior

In order to characterize wave propagation behavior, a swept sine wave (Figure 3) was input to the film specimen. Film specimen was subjected to the mechanical strain because it is expected that wave propagation behavior is influenced. Distance between a pulsar and a receiver was also verified.

Wavelet transforms of output signals are shown in Figure 4. Peak amplitudes of the signals are also indicated in the figures. In the figures for 3 mm, peak frequency is recognized around 800 kHz, which is equivalent to the peak frequency of used broadband transducer (NF, AE-900M). It can be seen in the figure that the attenuation of stress wave is significant. Comparing three figures for different applied strain, it was found that the influence of mechanical strain was negligible. It is worth noting that a large number of transverse cracks are initiated in the TCO layer until 5 % strain (see Figure 7). It is then understood that the cracking in TCO has little influence on the wave propagation characteristics.

Figure 4. Attenuation of AE wave due to the applied load and distance
3.2 AE behavior during tensile test

AE behaviors during tensile tests are shown in Figure 5. Figure 5(a) shows load, AE event rate and amplitude during tensile test for “Specimen A” for strain range of 0-3.0%. In the figure, bold line, dots and fine line indicate load, amplitude and AE event rate, respectively. AE event rate is defined as the number of AE signals per second. As seen in the figure, load increased monotonically and nonlinearly. The remarkable increase in AE event rate is recognized at the strain of ~0.8%. It reached a peak at the strain of ~1.2%, and then decreased. On the other hand, AE signals with low amplitude were detected before the remarkable increase in AE event rate and the maximum amplitude signal was detected at the strain of ~1.8%.

In order to identify AE sources in “Specimen A”, AE behavior during tensile test of PEN film (Specimen B) was investigated. Figure 5(b) shows load, AE event rate and amplitude during tensile test of “Specimen B” for the strain range of 0-3.0%. It is clearly shown in the figure that AE event rate was much lower and AE signals had quite small amplitude. Therefore, it is
suggested that the cracks were nucleated only in TCO layer.

### 3.3 Comparison of AE and electrical resistance measurement

Electrical resistance measurement was carried out to investigate the effect of damages on the electrical performance of TCO. Figure 6 shows load, AE event rate and electrical resistance during tensile test for the strain range of 0-1.0%. While the rapid increase in electrical resistance in TCO was observed at the strain of ~0.68%, the remarkable increase in AE event rate was recognized at the strain of ~0.63%. It is considered that the microcracks initiated and stably grew in short range, and the crack propagates through the specimen width unstably. The small stable growth of microcracks might be detected only by AE measurement. Consequently, it was demonstrated that AE monitoring is more sensitive to cracking in TCO than electrical resistance measurement.

### 3.4 Damage process of TCO

To identify AE sources, in-situ observation of specimen during tensile test with AE measurement was carried out using a digital microscope (Keyence, VHX-9000) placed in front of the specimen. The results of the tests are shown in Figure 7 (a) and (b). As shown in Figure 7(a), damage process in TCO under tensile strain was understood as fol-

![Figure 7. AE behavior and fracture process of tensile test of “Specimen A”](image)
1. Cracks transverse to the loading direction initiated in TCO at the strain of 0.67%.
2. The number of the cracks, then, rapidly increased to the strain of 1.97%.
3. It was saturated until the strain of ~9%.
4. Cracks parallel to the loading direction initiated in TCO at the strain of 9.63%.

On the other hand, as shown in Figure 7 (b), corresponding to stage 1, the remarkable increase in AE event rate was recognized at the strain of ~0.7%. AE event rate reached a peak at the strain of ~2% (stage 2). Corresponding to stage 3, AE event rate decreased. AE event rate increased again at the strain of ~10% (stage 4).

It was demonstrated by the observation that the strain when cracks initiated in TCO was almost same as the strain when AE event rate increased. For illustrating statistical characteristics of TCO cracking, the critical strain, which was defined as the strain at rapid increase in AE event rate, was investigated based on Weibull statistics. Weibull plot of the critical strain and photograph of edge of “Specimen A” are shown in Figure 8. As shown in the figure, the average value of the critical strain was 0.76%, and Weibull modulus (shape parameter) \( m \) was 22.0.

### 4. Conclusions

In this paper, tensile tests with AE monitoring of TCO deposited on PEN films used in DSCs were carried out. Electrical resistance was also measured to investigate the effect of damages on electrical performance of TCO. To identify AE sources, in-situ observation of specimen during tensile test with AE measurement was carried out. Finally, following conclusions were obtained:

1. Attenuation of AE signals in film specimen was significant. However it is not influenced by applied mechanical strain.
2. AE signals from damage in TCO were detected.
3. AE signals are more sensitive to cracking in TCO than electrical resistance.
4. Failure damage process of TCO + PEN films consists of the initiation of cracks transverse to the loading direction followed by their saturation and the nucleation of cracks parallel to the loading direction.
In this study, mechanical damage accumulation in TCO + PEN films used in DSCs under tensile strain was successfully monitored by AE technique. In future, to ensure reliability of DSCs, it is necessary to understand the damage mechanisms of individual components of DSCs such as TCO + PEN films coated with dye-sensitized porous TiO₂.

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