Investigation of Degradation Kinetics of Perovskite Solar Cells by Accelerated Aging

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Abstract—**The operational stability of encapsulated perovskite solar cells (PSCs) is imperative for their commercialization. Here, we have investigated the degradation of PSCs with organic (PTAA) and inorganic (NiO_x) HTLs under light and thermal stress. The device parameters under 1-sun illumination were monitored over time at different temperatures; 20 to 85°C. The device degradation kinetics has been discussed by adopting the Arrhenius model with temperature and humidity prefactor correction. The temperature-dependent device parameters analysis showed a lower value of degradation activation energy for the device with the PTAA (~0.274 eV) than that for the NiO_x device (~ 0.495 eV).**

Keywords—*Perovskite degradation, Arrhenius model, activation energy, device stability, humidity/thermal stress.*

I. INTRODUCTION

Perovskite solar cells (PSCs) have huge potential to be fabricated with cheaper materials and production costs than conventional semiconductor solar cells.[1] Despite the high device efficiency, the commercialization of PSCs is impeded by long-term stability. [2]–[4] The device under operation accelerates the loss of power conversion efficiency (PCE). The cause of operational instability of PSCs with different interface layers also largely remains elusive. Therefore, it is important to dig up the mechanistic parameters to track the degradation propagation.

An accelerating stress testing could provide a real picture of operational stability which is decisive for its commercialization.[1] The mean life time (MLT) of solar cell devices is carried out by accelerated life testing (ALT) under overstress conditions.[5] The most common stress conditions for ALT are:[6] (a) thermal stress followed by high temperature and/or temperature cycling and/or temperature gradients,(b) electrical stress with power cycling/voltage cycling/power extremes/voltage extremes, (c) mechanical stress with mechanical shock/stress/vibrational tests/creep-stress relaxation tests,(d) environmental stress i.e. humidity or radiation. Moreover, the ALT tests are also carried out by the combination of these tests. For example, thermal stress/humidity (typically T-85°C/*RH*-85%) or illumination/thermal stress conditions are popularly used for the testing of the different kinds of solar cells[6] including HaPCs.[7] Several reports have discussed the degradation of perovskite monitoring the device parameters and discussed the

different characteristics features.[8] However, the analysis of the degradation trend of device parameters has not discussed under ALT test conditions using an analytical model to explore the degradation kinetics.

In this report, we analyzed the degradation trend of the device parameters of PSCs under continuous illumination driven by thermal stress. ALT was performed at various temperatures *(20-85°C)* and under constant illumination of 1 sun. The device parameters monitored with time were fitted with a linear or exponential functional model to evaluate the degradation kinetics. The mathematical analysis revealed that the poor stability of the device with PTAA is attributed to a lower activation energy for degradation compared to the device with NiO_x.

II. EXPERIMENTAL

Device fabrication:

The details of the precursor solution and device fabrication can be found in the earlier reports.[9]–[12] In brief, for the fabrication of inverted PSCs, we have used ITO substrate and PTAA (2 mg/ml in CB) deposited by spin coating, NiO_x deposited by sputtering mentioned in our earlier.[10], [11] For the fabrication of perovskite films, we adopted two stept deposition PbI_2 deposition followed by dripping of the MAX precursor solution (a mixture of MAI + MACl.[9] For completion of device, PCBM as ETL, AZO layer and Ag. Devices were sealed by encapsulation glass and UV-curable resins (UV-RESIN XNR5516Z) before the subsequent measurement in ambient conditions.

For operational stability testing:

The encapsulated devices (PTAA and NiOx devices) in enclosed system under air ambient. The devices were kept under constant illumination and set temperatures (20, 60 and 85 °C). We have tested HaPSCs with two different HTLs; PTAA and NiO_x. During thermal stress, the devices were placed under constant illumination at relative humidity of 35-40% at room temperature in enclosed system.

The *J–V* scans were done every 7 h for the first 7 days and then once every 24 h until over 1000 h.

III. RESULTS AND DISCUSSION

To investigate the degradation kinetics, the PSCs with HTLs; PTAA or NiO_x were monitored under continuous illumination of one sun placing at thermal stress. The *J–V* characteristics of fresh devices are depicted in Fig. 1a. The PSC with the PTAA has a PCE of ~19.32% and the device with sputtered NiO_x has an efficiency of 15.60%. The characteristics

insights and have been discussed in our previous reports.[9], [11] The detail of degradation characteristics with the point of view of materials properties and interface quality has been documented in our earlier report.[13] In this report, we discussed the degradation kinetics of these devices under thermal and light stress considering the ALT model.
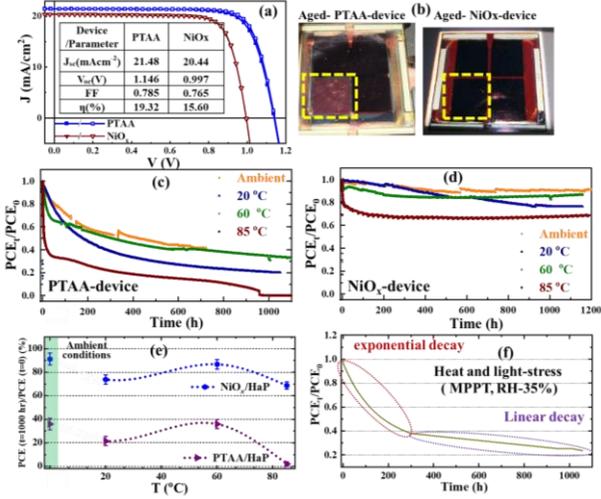

Fig. 1. Current density-voltage (J-V) characteristics of PTAA and NiO$_x$ devices (a). Photographs of aged devices after 1000 h (60°C) (b). The operational stability of the (c) PTAA/HaP and (d) NiO$_x$/HaP devices at different temperatures under maximum power point conditions (1 sun). (e) The relative performance of PTAA or NiO$_x$ devices aged under different thermal stress under continuous illumination. (f) Schematic display of degradation trend of PSCs showing exponential decay at the initial stage followed by linear decay. The shaded region indicates ambient conditions.

Figure 1b displays Photographs of aged devices of PTAA and NiOx devices. Figures 1c,d demosntrate the device degradation trend at 20, 60, 85 °C, and ambient conditions (27 °C<T<35 °C) under continuous illuminations (one sun) at RH of 35-40%for t>1000 h for respective devices. These devices showed a stark difference degradation rate. This is attributed to the difference in the interface chemistries at PTAA/HaP or NiO$_x$/HaP and HaP bulk with external stimuli. As given in Fig. 1e, the aged PSCs with NiO$_x$ retained ~74.8% of PCE$_0$ at 20 °C, 86.7% at 60 °C, 68.7% at 85 °C, and ~90.1% under ambient condition whereas the devices with PTAA device dropped to 22.5%, 35.9%, 2.0%, and 22.6% of PCE$_0$, respectively. The monitored data showed that the device parameters are primarily governed by the J_{sc} trend.

From the device stability data, we can notice that the J_{sc} of the PTAA/HaP device dropped faster than the NiO$_x$/HaP device. Particularly, an initial steep drop in PCE at 85°C was observed for both devices. A loss of fill factor in both devices is also affected by a gradual increase of the series resistance of the devices.

The degradation trend of the PSCs with either of HTLs followed by two characteristics functional regimes (Fig.1f). At the beginning, the degradation trend has the exponential decay which is followed by a linear decay. It is speculated that the rate of exponential or linear decay is influenced by the carrier transport layer used in the device configuration. Indeed, these trends are the consequence of collective effects of the partial

degradation of CTL, defect induced in HaP bulk by crystal phase transformation, and CTL/HaP interface.

A. Accelerated Degradation Testing Model

The degradation kinetics can be analysed by ALT models.[14] The Arrhenius model is a fundamental mathematical model for the analysis of optoelectronic device characteristics. The degradation constant for this model is given by:

$$k = Ae^{\left(-\frac{E_A}{K_B T}\right)} \tag{1}$$

Here, E$_A$- the activation energy, k$_B$- the Boltzmann constant 8.62×10^{-5} eVK^{-1}, T- the temperature in Kelvin and A - a constant dependent on the degradation mechanisms and the experimental conditions. The Arrhenius model primarily explains the kinetics of the temperature-dependent process.

To get more insights into the degradation kinetics under light and heat stress, the Arrhenius model equation (1) can be modified as:

$$K = \frac{k_{deg}(T_H)}{k_{deg}(T_L)} = \exp\left[\frac{E_A}{K_B}\left(\frac{1}{T_L} - \frac{1}{T_H}\right)\right] \tag{2}$$

where T_L and T_H correspond to low and high temperatures (reference temperature). In our analysis, we considered T_H=85 ^{o}C (standard temperature for reliability test). Note that a higher value of acceleration factor (K) denotes better device stability.
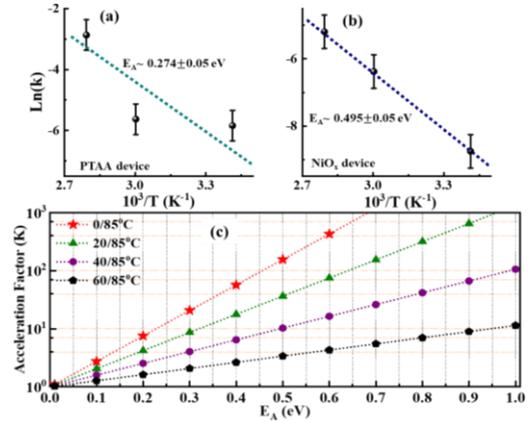

Fig. 2. The degradation activation energy of PSCs with (a) the PTAA and (b) NiO$_x$ estimated by analysing the trend of device parameters (J$_{SC}$). The estimation of acceleration factor of the device considering prefactor with the varying working low temperatures (T$_L$) with reference to the standard test temperature (T$_H$=85 ^{o}C) adopting the Arrhenius equation (1).

Since the J_{SC} degradation trend is parallel to the loss of PCE.[13] we analysed the J_{sc} trend at different thermal stress to calculate the degradation activation energy. The Arrhenius equation (1) was applied for the evaluation of the temperature dependence (Fig. 2a,b). It is found that the activation energy of the device with NiO$_x$ for degradation (0.495±0.02 eV) is higher than that of the PTAA device (0.274±0.02 eV). It indicates that the PTAA device, with lower activation energy, degrades faster. We found that the estimated values of E$_A$ for our devices are lower than Si, CIGS, or CdTe- based devices which are well-known for stable device performance with much higher MLT. It implicates that the value of E$_A$ is directly proportional to the MLT of PSCs. We believed that the difference in E$_A$ for the

PSCs with PTAA and NiO$_x$ is attributed to the structural defect in perovskite, interfacial deterioration of HTL/HaP, and HTL under heat and light stress. A lower value of E$_A$ for the PSC with PTAA could have stemmed from structural defect induced from thermal stress[15] and the partial deterioration of the PTAA film due to absorption of a high-energy photon under illumination. While higher activation energy for the device with the NiO$_x$ is analogous to the relatively stable device due to the robust nature of NiO$_x$ which results in a comparatively stable interface and immune to ionic diffusion for the perovskite bulk.

Furthermore, we have calculated the acceleration factor of degradation using equation (2) at working temperature (T$_L$) (T$_L$= 0 ℃ (winter), 20 ℃ (~below room temperature), 32 ℃ (~ ambient working temperature), and 60 ℃ (~working at the roof temperature) (Fig. 2c) with respect to 85 ℃. This result shows a higher acceleration factor at a lower working temperature. This means the MLT of the device is longer at a lower working temperature (T<85 ℃). Unlike the Arrhenius estimation, the experimental device data showed poor stability for T<20 ℃. It is to be noted that the environmental stress (temperature and ambient humidity) induces the defects such as structural defect and deterioration of interface or bulk layer used in device structures which could be the main factors for the anomalous trend (Fig. 1c, d).

IV. Summary and Conclusions

In summary, we investigated the light-heat stress accelerated degradation of PSCs with different interface layers. The degradation analysis of device parameters showed higher activation energy for PSCs with NiO$_x$ than PTAA indicating the interfacial effect on degradation potentials. The device degradation kinetics of PSCs can be described by the Arrhenius model with the introduction of temperature and humidity prefactor especially at lower working temperature (T<RT) while device stability at higher working temperature (T>30 ℃) follows the regular trend with temperature prefactor. This work corroborates that the degradation of PSCs can be slowed down by stabling the structural phase of HaP bulk and engineering the interfacial layer with higher activation energy.

Acknowledgment

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