Humidity and Moisture Degradation of Perovskite Material in Solar Cells: Effects on Efficiency

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Abstract: Humidity is the concentration of water vapor in air and moisture is the relatively small amount of water in a material. The two both have positive and negative influences on the development of perovskite solar cells. It is becoming increasingly clear that the effects of humidity will be a key factor to drive the commercialization of this promising new solar cell technology. The interface amid MAPbI₃ and water vapor has been explored and studied by different researchers through optical absorption spectrometry, morphological and crystallographic studies. These studies have helped to demystify the complex interactions going on in the system. A particular study reported the possibility of a perovskite molecule forming a hydrate compound when exposed to H₂O vapor in the dark coupled with its dissolution of MAPbI₃. Some researchers have said that to improve the stability of this device in moisture. The device must be studied as a whole system rather than studying just the individual components. This review paper explores the works done on perovskite stability highlighting how humidity and moisture affect both the preparation and performance of perovskite material and perovskite solar cell.

Keywords: Degradation, Moisture, Humidity, Perovskite

1. Introduction

Recently, different kinds of perovskite solar cell (PSCs) material have been explored attributable to the promising power conversion efficiency perovskite materials and devices are showing and their affordable production costs [1]. There has been a rapid rise in the photovoltaic potential of perovskites within just 7 years. However, the challenge perovskite
faces are its stability in industrial applications[2]. A major source of degradation for perovskite is through the decomposition of chemical constituents of the material in unfavorable environmental conditions. Possible solutions for this problem have been adopted such as encapsulation techniques for the organic material. Still, the long-term solution can only be discovering new perovskite materials and better fabrication techniques that will aid stability[3]. This new hybrid perovskite structure ABX$_3$ (usually A=CH$_3$NH$_3$ (MA) or NH$_2$CHNH$_2$ (FA); B=Pb or Sn; X= Cl, Br, I or mixed halides) that has achieved as high as 22.1% power conversion efficiency with low production costs and as a result of their optical and electronic properties have also experienced drawbacks such as voltage hysteresis, light soaking, ionic migration, heavy metal lead and long term stability [4].

Humidity is the concentration of water vapor in the air and relative humidity is used to refer to the amount of humidity as a percentage. Moisture is the relatively small amount of water diffused in a material. The reason for instability of perovskite is the hygroscopic character of the organic ammonium starting material and metal salts solubility in unfavorable environments [5]. This unfavorable condition is usually during high humidity and moisture content in the atmosphere. Other possible causes of degradation are thermal decomposition, bias-induced ion migration, light-induced trap state formation and phase transition[6][7], [8]. Several recent studies have highlighted the degradation mechanisms of perovskite both intrinsically and extrinsically for various structures and materials and have suggested some ways to improve stability [9]. Faming and Mingzhen reported that the perovskite material self-stability can be improved through mixed halide and cation doping, finding inorganic charge transport materials that are moisture-resistant and modifications of PSCs interfaces can be explored to mitigate the instability of perovskite materials in humid and moist environments [1], [10]. Moisture is said to have a positive impact on MAPbI$_3$ at the annealing stage, but its effects in other stages and different perovskite films remain uncertain [11][12]. It was reported that moisture harmed the nucleation of perovskite films during spin coating while enhancing the crystal growth at the annealing stage for organic-inorganic lead perovskite films by Gao et al [13].
2. Experimental

A study was performed to reveal how humidity affects the preparation of perovskite films. To achieve this, we first distinguish how humidity affects the deposition step and preparation stage. For the preparation stage, different levels of humidity were used in preparing the perovskite film (triple-cation) in the presence of two kinds of nitrogen (dry and humidity saturated) to yield relative humidity values of 0%-40%. The deposition of the perovskite film was subsequently done using a no-solvent approach along with other layers. Contreras-Bernal et al. reported the merits of the presence of water in a perovskite material which helps resist degradation in humid environments. The XPS analysis carried out showed that the presence of very little quantity of water, which formed a coordination sphere around the Pb cations. This coordination sphere prevented any form of additional hydrates that could trigger degradation [14]. Hashmi et al. stated a post-treatment of carbon-based printed perovskite solar cells using humidity-assisted thermal exposure. The humidity thermal exposure treatment had positive impacts on the several layers of the PSC by improving their photovoltaic potential [15]. Zhu et al. performed an in-situ environmental test by using water vapor to control relative humidity. This was carried out to determine the dissolution and recrystallization process of Cs₂SnI₆. The vapor pressure was increased at a constant rate of 20pa/min to 1000pa (Relative Humidity= 58.5%) and subsequently, at a rate of 10pa/min to 1660pa. At constant pressure, crystal dissolution was allowed to occur for 20min. Before the pressure was reduced to 715pa at a constant rate of 10pa/min [16]. Xu et al. stated that the presence of moisture in perovskite films under 60% relative humidity is not problematic for the production of very efficient perovskite solar cells [11]. Christian et al. studied how MAPbI₃ and H₂O vapor would interact without illumination and discovered the formation of (MA)₄ PbI₆.2H₂O. This changed the crystal structure of the material and effectively reduced the perovskite material light absorption potential [17]. According to Habiserreutinger et al., irreversible decomposition of the dihydrate phase occurs faster in perovskite cells stored under illumination than the ones stored in dark conditions [18].
Figure 1. Shows the scanning electron micrographs for perovskite material films kept in a dark environment at 25 °C and 0%, 50%, 90% Relative Humidity for 14 days. Samples (A-C) taken after perovskite deposition while samples (D-F) kept in dark conditions for 14 days[17].

3. Results and discussion

Perovskite solar cells kept at 90% humidity showed a fast reduction from 12% to <0.7% in photovoltaic performance within just three days. Some cells kept at 50% and 0% humidity had better stability with a less than 5% loss in photovoltaic performance within 21 days [17]. Wang et al. reported in 2016 that the stability of perovskite should not be focused on perovskite material alone or the factors affecting the perovskite material. Rather efforts should be made to understand how the device as a whole system interacts regarding stability[19]. Also, they reported that perovskite film absorption edge occurred at 1.57 eV initially, but after 20 hours of exposure in the humid environment, there was a double reduction of absorption within the range of 1.5 to 2.5 eV. A shift to 2.3 eV in the absorption edge is caused by the formation of PbI₂. This also validates the change in color from dark brown to pale yellow on exposure to humidity [19]. Leguy et al. suggested that in the presence of water vapor permanent decomposition of MAPbI is
possible if the grain is completely transformed to the monohydrate phase\cite{20}. Leguy et al. determined the time-dependent changes to MAPbI films exposed to moisture using thin-film ellipsometry measurements and the single-crystal optical constants. The outcome revealed the formation of a monohydrate phase irrespective of the film depth, permitting fast movement of water molecules along the boundaries of perovskite film grains. While the unencapsulated solar cells at the vapor hydration phase initially at \(V_{oc} = 1.05\) V and \(J_{sc} = 10\) mA cm\(^{-2}\) at 1 sun lost \(\sim 200\) mV in open-circuit voltage and dropped 90% in short-circuit photocurrent \cite{20}. The difference between alterable and unalterable degradation is in the presence or absence of condensed water in the perovskite material film. When there is an absence of condensed water the reaction can be reversed simply by blow-drying as suggested by Leguy et al.

The relationship between the annealing time and ambient humidity of perovskite solar cells for optimum performance was studied by Cronin et al. The results showed that moderate humidity and moderate anneal time was the best combination to achieve optimum performance. Low humidity and short anneal time caused the incomplete conversion of the perovskite material while long anneal time and high humidity caused porous film morphology coupled with chemical degradation \cite{21}, \cite{22}. For future industrial scale-up of this technology, knowledge of the required humidity will be very important. Wei et al. described the use of a water-resistant perovskite absorption layer for enhanced stability of perovskite by utilizing a supramolecular macromolecule to form supramolecular interactions with the organic cations through the hydrogen bonding present in the perovskite films \cite{23}–\cite{25}. The \(\beta\)-cyclodextrin (\(\beta\)-CD) supramolecular macrocycle that was used helped improve the ambient condition stability of PSCs and consequently the photovoltaic performance. Furthermore, the supramolecular macrocycle \(\beta\)-CB also enhanced the crystalline characteristics of the perovskite films, therefore, protecting the perovskite films under from moisture defects\cite{23}. An efficiency of 20.09% was achieved by adding this \(\beta\)-CD material to the perovskite film.

It was discovered that from 0%-10% relative humidity the performance of the PSC was relatively stable. But from 10% upward the perovskite solar cell started experiencing a decrease in open-circuit voltage \((V_{oc})\) and short-circuit current density
(J_sc). This suggests that until 10% of relative humidity PSCs can be produced with no performance changes [26]. Salado et al. studied how moisture-induced degradation affects perovskite solar cells. It was uncovered that the charge recombination mechanism was altered in the presence of moisture. After moisture exposure, there was an additional mid-frequency recorded which infers the accumulation of interfacial charge. This interfacial charge accumulation could speed up the rate of charge recombination as a result of a more surface-mediated recombination route [27]. Fu et al. stated the relationship between moisture degradation of perovskite material and the formation of methylammonium salt and lead halides from MAPbI_3 and how removal of metal halides would equally increase perovskite degradation [28]. When perovskite material is exposed to H_2O it acts as a Lewis base CH_3NH_3PbI_3 forms a coordinated intermediate [(CH_3NH_3)^\text{+}\n\text{-}\ 1(CH_3NH_2)nPbI_3][H_2O] with H_2O, which then reduces the perovskite stability and performance [29]. Kim et al. stated that the perovskite layer had low moisture resistance and noted that asthma challenge that have delayed the development of perovskite solar cells [30]. Shahbazi et al. described the reaction of a water molecule and MAPbI_3 crystal structure which already has one water molecule to form MAPbI_3.H_2O as follows:

$$\text{MA}_4\text{PbI}_6.2\text{H}_2\text{O(s)} + \text{H}_2\text{O} \rightarrow 4\text{MAI (aq)} + \text{PbI}_2(s) + 2\text{H}_2\text{O}$$ (I)

As the perovskite is further exposed to humidity the perovskite structure takes up another water molecule and therefore a new structure is formed with two molecules of water. When the perovskite structure is in the dihydrate phase the excess water may cause the MA^+ to dissolve which creates an unalterable degradation mechanism of the perovskite molecule as shown in the equation above [31]. This is also in agreement with the theory of acid-base reaction proposed by Frost et al. as a likely route for the decomposition of perovskite material with moisture present and under illumination [29].

Planar methylammonium lead iodide PSCs were studied for stability at high temperature and humidity using encapsulation technique and it was discovered that encapsulated devices had decent performance at room temperature and zero humidity but then degradation was observed at higher temperature and humidity. The stability in
moisture was further improved by employing the OLED technology for sealing of the devices and it effectively reduced moisture from entering the cell at higher temperatures [32], [33]. Noh et al. investigated the how stable MAPb(I_{1-x}Br_x)_3 hybrid solar cells are with several compositions (x=0, 0.06, 0.20 and 0.29) under suitable limits with regulated humidity and different length of time as shown in the figure below. The result showed no substantial degradation at <50% RH, but beyond that MAPbI_3 began to degrade, with the color change observed (dark brown to yellow). Furthermore, the composites were stored at 35% RH while the MAPbI_3 composites were exposed for a day at 55% RH. Significantly, the MAPb(I_{1-x}Br_x) (x=0, 0.06) degraded seriously while (x=0.20, 0.29) stained their PCE. This proves that MAPbBr_3 is more stable than MAPbI_3 when exposed to moisture [34].

Figure 2. Shows the XRD graphs for lead iodide, CH_3NH_3PbI_3 films at 0%, 50%, 90% RH at 0, 28 and 7 days respectively and (CH_3NH_3)_4PbI_6.2H_2O crystals [17].

The patterns prove that at high humidity the perovskite experiences rapid hydration as seen in (d) and confirmed in (e).
Figure 3. Shows the power conversion efficiency for a heterojunction MAPb(I_{1-x}Br_x)\(_3\) (x=0, 0.06, 0.20, 0.29). At 35% RH and subsequent exposure to 55% RH for performance variation analysis\[34\].

4. Conclusion

In conclusion, humidity and moist environments hurt perovskite solar cell devices performance by 0.2% and 0.12% respectively. This has been proven as detailed by all the papers review herein. This effect humidity has on perovskite can be managed and handled properly if regulatory actions are considered when fabricating these solar cell devices. With the current technology available and present knowledge about perovskite, it is best to keep explore better perovskite materials that can handle high humidity conditions. This coupled with improved fabrication techniques can be very necessary to improve the effects of humidity on perovskites.

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