A brief review on the moisture stability for perovskite solar cells

Hongming Xu¹,a

¹College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China.
auxuhongming2020@163.com

Abstract. Perovskite solar cells have attracted lots of attention in recent years with the power conversion efficiency increasing from an initial value of 3.8% up to 25.2%. However, its large-scale commercialization still faces various challenges, among which stability issue is the key to this process. Herein, we briefly reviewed the mechanism of perovskite material deterioration in the influence of water erosion as well as several effective strategies reported in recent years to improve the wet stability of perovskite solar cells, such as the composition engineering, surface passivation, dimensional design, etc.

1. Introduction

Among all kinds of photovoltaic technologies, perovskite solar cells are under the spotlight. In 2009, Miyasaka et al. first applied organic lead halide perovskite in liquid dye-sensitized solar cells, achieving a conversion efficiency of 3.8%. However, since the liquid electrolyte tended to corrode perovskite materials, Kim et al. used spiro-OMETAD, an organic solid material, as the hole transport material to replace the electrolyte and fabricated solid perovskite solar cells for the first time in 2012. The device PCE increased to 9.7%. After years of extensive research, the PCE of perovskite solar cells have reached up to 25.2%.

The general formula of perovskite is ABX₃, where A is generally an organic cation, such as CH₃NH₃⁺ or CH(NH₂)₂⁺; B is generally Pb²⁺, Ge²⁺, Sn²⁺; X is usually a halide ion such as I⁻ and Br⁻. The main advantage of perovskite solar cell is its high efficiency, which is comparable to that of the silicon-based single junction device. Besides, the device preparation process is simple with low cost. However, there are still some unresolved problems that restrict the large-scale commercial application of perovskite solar cells, among which the stability issue is a key challenge. There are several environmental factors that can influence the device stability performance, such as moisture, light, thermal stress and electric field. Herein we mainly focus on the moisture stability issue for perovskite solar cells and briefly discussed several strategies to enhance the device stability against moisture.

2. Degradation mechanism of perovskite solar cells in a humid environment

Perovskite solar cells are currently facing the problem that they cannot be used in a wide range of industrial applications due to their poor chemical stability under the stress of environmental factors such as ultraviolet (UV) light, oxygen, heat and moisture, etc. As mentioned above, in this review we mainly focus on perovskite solar cell’s moisture stability. The moisture stability issue of perovskite solar cells based on the vastly applied and studies materials CH₃NH₃PbI₃ is mainly reflected in the following aspects. First, CH₃NH₃⁺ has the ability to provide protons and in the presence of water, it will take one of its protons and make itself into an intermediate [(CH₃NH₃⁺)ₙ₋₁(CH₃NH₂)PbI₃][H₂O]. Moreover, this
intermediate is unstable, which can be further decomposed into HI, CH$_3$NH$_2$ and eventually PbI$_2$. This change can be seen directly with eyes because CH$_3$NH$_3$PbI$_3$ is dark brown and the decomposition product PbI$_2$ is yellow. Figure 1 shows the specific process.

\begin{align}
\text{CH}_3\text{NH}_3\text{PbI}_3 (s) & \leftrightarrow \text{PbI}_2 (s) + \text{CH}_3\text{NH}_3\text{I} (aq) \quad (2a) \\
\text{CH}_3\text{NH}_3\text{I} (aq) & \leftrightarrow \text{CH}_3\text{NH}_2 (aq) + \text{HI} (aq) \quad (2b) \\
4\text{HI} (aq) + \text{O}_2 (g) & \leftrightarrow 2\text{I}_2 (s) + 2\text{H}_2\text{O} (l) \quad (2c) \\
2\text{HI} (aq) & \leftrightarrow \text{H}_2 (g) + \text{I}_2 (s) \quad (2d)
\end{align}

**Fig.1** The decomposition process of CH$_3$NH$_3$PbI$_3$ in the humid ambient environment. Reproduced with permission. Copyright 2019, SPIE-SOC

3. Strategies to enhance perovskite solar cells’ stability against moisture

Many research groups have made efforts to solve perovskite instability issue in ambient environments. In the following section we will discuss several approaches which are considered to be feasible and innovative in this field.

3.1 Composition engineering

Early research has showed that composition engineering was an effective method to enhance perovskite moisture stability in the traditional perovskite system such as MAPbX$_3$.

Seok et al. fabricated both MAPbI$_3$ and MAPb(I$_{1-X}$Br$_X$)$_3$ as the light harvester in perovskite solar cells. When they placed both in the ambient conditions with a relative humidity over 55%, they found that the color of the original MAPbI$_3$-based perovskite film changed from dark brown to yellow. In contrast, the color of the MAPb(I$_{1-X}$Br$_X$)$_3$ hybrid perovskite film did not change significantly. The authors reasoned that the stability improvement of MAPb(I$_{1-X}$Br$_X$)$_3$ perovskite was related to its more compact and stable crystal structure compared to the pristine one, since the replacement of large I$^-$ ions with small Br$^-$ ions could result in smaller unit cells, stronger interactions, and the easier formation of cubic phases.

In 2016, Xia et al. also introduced Cs into FAPbI$_3$ perovskite to obtain perovskite with FA$_{1-X}$Cs$_X$PbI$_3$ structure. They compared the performance of the battery at different doping amounts of X, and found that the PCE reached a maximum of 14.9% at X=0.1. The reason is that doping Cs is beneficial to the growth of large crystal particles. The average grain sizes of FA$_{0.9}$Cs$_0.1$PbI$_3$ film is 257nm, which are the largest among the groups. According to previous research, large crystal particles can improve the crystallization and reduce perovskite membrane crystal interfaces, which is advantageous to the carrier transportation. After that, they also placed the unencapsulated FA$_{0.9}$Cs$_0.1$PbI$_3$ and pure FAPbI$_3$ in the external environment with a relative humidity of 50% and a temperature of 20°C for 100h. The devices
doped with cesium still retained their original dark color, while the undoped devices turned into yellow. The PCE of pure FAPbI$_3$ decreased from 11.4% to 0.35%. In contrast, FA$_0.9$Cs$_0.1$PbI$_3$ decreased from 14.2% to 12.5%. Similar work based on the FA$_{0.85}$Cs$_{0.15}$PbI$_3$ perovskite was conducted by Zhu et al. After being placed in an environment with a relative humidity of 15% for 30 days, there was no significant change of PbI$_2$ peak and δ-phase peak in the XRD pattern of this material. To a certain degree, it reflected its stability. Through the partial incorporation of Cs, the original cell volume is reduced. Thus the interaction between FA and I is enhanced leading to less sensitive to water.

3.2 2D perovskite

The general structural formula of Ruddlesden-Popper 2D perovskites is (RNH$_3$)$_2$An-1MnX$_{3n+1}$ (n=1,2,3,...)\(^{11}\), where RNH$_3$ generally refers to a larger aliphatic or aromatic alkylamine cation and the other remaining components are similar to those in 3D perovskites. Different from the three-dimensional spatial network structure composed of octahedral [MX$_6$]$^{4-}$ in 3D perovskite, 2D perovskite is more like a sandwich structure, connecting different layers through these large space cations. This type of perovskites has been widely reported for its improved photoelectric performance, especially the outstanding stability.\(^{12}\) Mohite and Kanatzidis et al.\(^{13}\) prepared a thin film with a quality close to single crystal by the hot-casting (HC) technique. This film has shown outstanding ability in charge transferring. Therefore, the photoelectric performance of the solar cell was greatly improved with PCE increased from 4.02%\(^{14}\) to 12.52%. More importantly, the device also had outstanding stability. They conducted wet resistance tests on unencapsulated 2D and 3D perovskite-based solar cells respectively. In an ambient environment with a relative humidity of 65%, the performance decay rate of 2D perovskite solar cell was significantly lower than that of 3D one. After that, they also conducted relative tests for the encapsulated device. After aging for 350 hours in the same environment, the PCE of 3D perovskite solar cell dropped to less than 10%. In comparison, 2D cell didn’t experienced such a severe performance degradation after 650h.

Unlike the conventional application of BA$^+$ in the past, Ziqi Liang et al.\(^{15}\) chose to use iso-BA$^+$, a molecule with short branched chains, as spacer cations. They also adopted the hot-casting (HC) technique to prepare the (iso-BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ 2D perovskite cell. Through the test, the performance of the iso-BA$^+$-based device was superior to the BA$^+$-based one in nearly all aspects. After ageing in an ambient environment with 60% relative humidity at 20℃, the modified device without encapsulation could still maintain its original color after 840h. What’s more, the PCE for the optimized device could rise up to 10.63%.

3.3 Surface passivation

3.3.1 Organic passivator

Jinsong Huang et al.\(^{16}\) used the quaternary ammonium halides (NR4$^+X^-$) as the passivation layer. In the hydrophobic protective material test, they applied a passivation layer consisting of choline chloride and L-α-phosphatidylcholine on a perovskite FA$_{0.83}$MA$_{0.17}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ device. At ambient atmosphere with a relative humidity of 50-85%, the device based on the choline chloride was aged for nearly a month and could still maintain nearly 100% battery efficiency. Despite the hydrophobicity of the long-chain molecules, the efficiency of solar cells modified with L-α-phosphatidylcholine decreased by nearly 30% after aging for 800 hours. They then conducted another experiment to confirm this conclusion based on the color change of the following three kinds of perovskite films: the original film, the choline chloride modified one, and the L-gluco-phosphatidylcholine modified one. All three groups were exposed to the air with relative humidity of 90±5% for 2.5 hours. At the beginning, the color for all three kinds of films were dark brown. After 2.5 hours, the dark color of the original one faded and turned yellow obviously. L-alpha phosphatidylcholine modified perovskite film only showed a little yellow part, while for the choline chloride-based one, none obvious color change was observed with naked eyes.
Another interesting work is that Kazunari Matsuda et al.\textsuperscript{17} prepared perovskite solar cells by spraying the surface of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} with poly (methyl methacrylate) (PMMA). This polymer layer can effectively separate the hole transport layer from the electron transport material, reducing the trap density of perovskite materials. As a result, it could effectively prevent carrier combination and improve the efficiency of solar cell over 18\%. They also found that the material improved the solar cell’s water resistance ability. In the ambient environment with relative humidity of 70\% and at 298K, the PCE of solar cells without PMMA additive decreased significantly within 20 days with value less than 80\% of the original one. By contrast, the solar cell with PMMA polymer still maintained more than 94\% of the original efficiency. Then they researched its morphology with a scanning electron microscope (SEM). By comparing the SEM images, it could be clearly observed that there were many pinholes in the film of the reference sample, while there was relatively fewer pinholes in the sample modified by PMMA.

What’s more, Dinesh Kabra et al.\textsuperscript{18} prepared a perovskite solar cell based on bathocuproine (BCP) additive. In droplet contact angle test, they found the contact angle for water with pure perovskite film was 52° which was much lower than the perovskite with BCP added (up to 85°), which indicated a better hydrophobic property. This may be derived from the large pyridine and alkane groups in the BCP structure which have strong water resistant ability. In order to further explore the possible changes during the process, they placed the solar device with/without BCP in the ambient environment with relative humidity of 45 ± 5\% for 15 days, and then carried out XRD detection. From the XRD pattern, they identified that the cell without BCP had obvious peaks of PbO and CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}(H\textsubscript{2}O). However, the other one with BCP did not have any new peaks appearing. These results undoubtedly confirmed that the addition of BCP could improve the moisture resistant stability of perovskite. Based on a similar approach, Jin Zhang et al.\textsuperscript{19} used another organic material oleic acid (OA) as a passivation layer on the perovskite surface. Solar cells with/without OA were tested in an ambient environment with a relative humidity of 76\%. After one week, the complete degradation of perovskite film without OA treatment was detected based on the UV-Visible light spectrum. However, the absorption curve of perovskite film treated with OA showed only a slight decrease after four weeks, indicating that only a mild degradation occurred. The film color change (from dark brown to yellow) also highlighted OA could improve the water resistance ability. Interestingly, they also found that the device performance with OA was slightly better than that without it. This might be attributed to large alkyl groups of OA, which could increase the distance between the two interfaces and reduce the probability of carriers recombination.\textsuperscript{20} Qingbo Meng et al.\textsuperscript{21} applied polystyrene (PS) in the perovskite solar cells, which could stick tightly to the outer surface of the film, prevent environmental erosion and impede the degradation process. PS material had been proved to have not only excellent thermal stability, but also excellent water resistance. Due to the excellent hydrophobicity of PS, the water contact angle for the PS-free film was 69.4°, whereas film with PS was significantly larger, up to 104.9°. The coating layer could effectively inhibit water from reaching the active layer. In the subsequent experiment, the perovskite films with/without PS were placed on the top of hot water and hot steam for the degradation test. Although the colour of the film protected by PS began to change within 8 seconds, the film without PS changed significantly faster within a second. This result also proved that PS could effectively prevent water erosion. Similar results were observed when the prepared film with/without PS protective layer was placed in isopropanol. Interestingly, the researchers found that as time went by, the color of the PS-film gradually changed back from yellow to dark brown, indicating that it had excellent self-healing ability.

3.3.2 Inorganic passivator

Rui Zhu et al.\textsuperscript{22} made use of the characteristics of tetraethyl enololruthosilide (TEOS) hydrolyzed in water to produce silica oligomers (the specific reactions are shown as follows\textsuperscript{23,24}). They mixed TEOS with Formamidinium (FA) type perovskite precursor solution (Figure 2a). The silica oligomers hydrolyzed by TEOS could co-deposit with perovskite crystals to form a nano-scale composite film, as shown in Figure 2b-c.

\[
\text{Si(OC}_2\text{H}_3)_4 + 4\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 + 4 \text{C}_2\text{H}_5\text{OH} \quad (1)
\]
\[
n\text{Si(OC}_2\text{H}_3)_4 + n\text{Si(OH)}_4 \rightleftharpoons (\text{SiO}_2 \ldots \text{SiO}_2)^{n-} + 4n \text{C}_2\text{H}_5\text{OH} \quad (2)
\]
They conducted several kinds of moisture ability tests on FA$_{0.85}$Cs$_{0.15}$PbI$_3$-based solar cells with/without special treatment of TEOS. The solar cells were aged in an ambient environment with a relative humidity of 80% at 25°C. After 2 hours, the XRD pattern showed the new peaks representing the phase transitions in the reference sample and the wavelength change in the UV-visible absorption spectra also confirmed the conclusion. But when they analyzed the solar cells modified with silica oligomers, they could not see any new peaks of the related compounds on the XRD pattern, indicating that the original FA$_{0.85}$Cs$_{0.15}$PbI$_3$ peak was basically intact. There was no significant wavelength change in the same UV-visible spectra, either. These experiments have undoubtedly proved that this self-assembled inorganic hybrid film can improve the water resistance of perovskite solar cells. Moreover, its preparation process is relatively simple with low cost, making it a potential method to prevent the water-caused degradation for perovskite solar devices.

![Fig.2](image_url)

**Fig.2** (a) Mixed TEOS with formamidinium (FA) type perovskite precursor solution. (b) TEOS hydrolyzes into silica oligomers. (c) Schematic illustration of the silica oligomers co-deposits with perovskite crystals to form a nano-scale composite film. Reproduced with permission. Copyright 2018, Wiley-VCH.

### 4. Summary

Although the efficiency of perovskite solar cells has increased dramatically in recent years, the stability issue has been a problem remaining to be well solved. Water molecules in the ambient environment can react irreversibly with the active layer of the perovskite cell and promote its degradation, which leads to the device instability during its long-term operation. After exploring the possible mechanisms, scientists have come up with various strategies to deal with it. First of all, by applying different anions and cations in the precursor, the interaction force in the unit cell can be improved and the perovskite crystal structure can be stabilized. This method can usually enhance device power conversion efficiency as well as wet stability simultaneously. The key in this method is to find the optimized stoichiometric ratio in the precursors. Secondly, some large organic cations carrying long chains can be introduced to prepare 2D perovskite. The 2D perovskite itself has good hydrophobicity, which can effectively prevent water erosion. In addition, the interface passivation strategy has gradually become one of the most popular methods to improve the wet stability in recent years. There are a lot of defects on the perovskite surface and grain boundary. These defects are often the cause of active layer degradation and the decrease of the solar cell efficiency. Therefore, adding a passivation layer between perovskite and carrier transport layer can improve the device efficiency and wet stability at the same time. Finally, we can use encapsulation process to effectively prevent water molecules from eroding the solar cell. However, this kind of palliative method will inevitably increase the fabrication costs and cannot fundamentally solve the problem. Although all these above methods can improve the lifetime of the solar cells from a few
dozen hours up to over 1000h, it does not still meet the requirements of long-term stable operation of the solar cell according to the industrial standards. Perhaps in the future, this goal can be achieved by improving the stability of perovskite structure together with external encapsulation assistance. But for now, there is still a lot of work to be done for perovskite solar cells to surpass commercially available silicon-based solar cells.

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