

Advances and Challenges When Commercializing Perovskite Solar Cells

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Abstract. Currently, the perovskite solar cells efficiency exceeds 20% at a rate of improvement that is unprecedented. This technique is indeed very promising because it is compatible with inexpensive solution processing. To be commercially viable, a thin-film solar device must pass the International Electrotechnical Commission (IEC) testing standards for environmental stability. Commercialization of perovskite solar cells is now restricted by lack of stability. The primary cause of this issue is the perovskite layer instability when exposed to moisture, light, and thermal variables. Nonetheless, it is crucial to investigate stability issues within device's layers and interfaces. Due to the interdependent relationships between the layers, including the charge transport layer, and electrodes, it is necessary to approach the device as a whole system in order to address the stability challenges described in this article. Future study should concentrate on strengthening the perovskite's intrinsic stability, engineering the device shape, and identifying durable encapsulation materials that resolve extrinsic instability and seal the device against moisture for perovskite solar cells to reach the requisite stability.

Keywords: Perovskite, photovoltaics, stability, degradation, commercialization.

1. Introduction

The hunt for conventional energy sources for the future has been spurred by environmental issues and limited supply linked with existing energy sources. Renewable energies have emerged as an attractive option for addressing energy demands in a sustainable and cost-effective manner. The global installation of hydropower generators, wind turbines and solar photovoltaic modules totals tens of gigawatts. Solar photovoltaics (PV) technology, which converts sunlight into electricity, promises a possible path for the generation of approximately one-third of the world's energy in the foreseeable future. Perovskite solar cells (PSCs) are a priority for solar cell research due to their rapid increase in efficiency and simplicity of mass production among PV technologies. In 2009, it was categorized as a sensitized solar cell with a power conversion efficiency (PCE) of 3.81% [1]. Today, laboratory-scale devices have an efficiency greater than 25.7% [2].

The term "perovskites" is used to name a group of substances with general formula of ABX_3 . A refers to a cation, B refers to a metal cation, and X is an anion of a halide. Essentially, calcium titanium oxide ($CaTiO_3$) is the primary constituent of perovskite. In 1939, Gustav Rose discovered this mineral in Russia's Ural Mountains. Further study was conducted by a Russian mineralogist, Count Lev Alekseevich Perovski (1972–1856), the term "perovskite" is then named after him. However, it has recently been used with exceptional success to the field of photovoltaics. In the science of photovoltaics, an organic–inorganic metal halide ($CH_3NH_3PbI_3$) perovskite (hereinafter shorten to perovskite) that has been the subject of the most research. The most commonly encountered perovskites consist of methylammonium ($CH_3NH_3^+$), lead (Pb^{2+}), Sn, FA, Cs and a halide (I^- , Br^- , or Cl^-) or mixture of halides, etc.

However, considerable technological obstacles must be overcome before perovskites may be commercialized in the energy sector. Stability is the greatest technological risk for perovskite photovoltaics, which necessitates the improvement of its resistance to varied environmental conditions. Numerous scientists have devoted significant effort aim to improve the stability of perovskite solar cells. It is importance to understand the degradation pathways when creating therapies for the variables responsible for degradation. Perovskite solar cells consist of multiple layers. the objective of this review is to take a fuller overview of the causes behind the device's instability.

In the first part, several perovskite and PSCs degradation mechanisms are reviewed, such as the moisture and oxygen effect, thermal effect, and illumination impact. In the second section, some strategies for strengthening the stability are addressed, which shows the interrelated nature of the instability of the multiple layers, and the effect of various device geometries.

As PSCs are explored for commercial uses, there must be defined methodologies for evaluating the device's reliability and dependability. The International Electrotechnical Commission (IEC) establishes criteria for testing the stability and dependability of PSCs that can be considered a standard [3]. The solar technological potential of perovskites is significant. It has capacity to build a low-cost, high-efficiency module in the commercial power sector, featuring network speeds and energy payback lengths superior to those of current PV systems. In order to optimize perovskite's potential in the solar energy industry, the US Department of Energy Solar Energy Technologies Office (SETO) urges the perovskite community members to increase device size, prove considerable outside endurance, and make stable processes [3].

2. Structure and Properties

2.1. Structure

As mentioned above, the compounds with the general structural formula ABX_3 are recognized as perovskites, A and B are both cations, where X is a halogen anion normally. Even though perovskite materials have been utilized in several fields to date, two kinds of halide perovskites are widely used in solar cell devices: (a) Organic-inorganic halide perovskites and (b) Alkali, which has Methylammonium ($CH_3NH_3^+$) as its cation, is the perovskite utilized most frequently in solar cell devices to far. If it meets Goldschmidt tolerance and octahedral stability-determining parameters, an ideal perovskite should be structurally stable.

Goldschmidt's tolerance factor (t) was formulated to illustrate perovskite structure previously. Nowadays, it is used for determining the ionic crystal structure stability too, $t = (r_A + r_B) / (\sqrt{2}(r_B + r_O))$. Usually, A- site cations were bigger than B- site cations ($r_A > r_B$). The tolerance factor generally ranges between 0.75 and 1.00 for all perovskites. It lies between 0.9 and 1.0 for perovskites have cubic structure, while any value outside of this cubic range verifies the hexagonal, tetragonal orthorhombic, and rhombohedral structures.

2.2. Photoelectric properties

The perovskite materials which are halide-based regarded as favorable for solar cell applications because of their desirable features, for example, tunable band gap, high coefficient of absorption, acceptable electron and hole transport, larger diffusion carrier length and electron mobility, reduced exciton binding energy and surface recombination velocity, longer carrier life span and photoluminescence, and improved structural defect tolerance. By manipulating the concentration of constituent cations and anions as well as the perovskite material's size and shape, it is possible to customize these features for use in the perovskite solar cells construction.

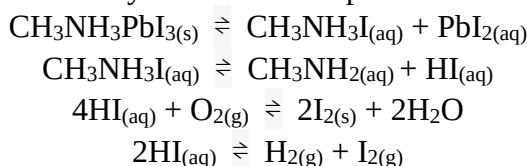
3. Degradation in PSCs

Due to their appealing characteristics, perovskite solar cells have garnered significant interest. However, the life span of PSCs is still a concern, where silicon solar cells have a lifespan of 25 year, but PSCs can only last for one year. Numerous factors, including as moisture and oxygen, temperature instability, light, and toxicity, influence the stability of PSCs. In the sections that follow, the effects of the aforementioned components are described briefly.

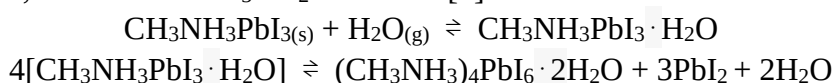
3.1. Oxygen and moisture effect

Water on its own and in contact with oxygen is a quite significant widespread factor influencing perovskites. Due of their capacity to cause solvation, water and other polar solvents may affect

perovskite. Via adjusting deposition techniques, polar solvents can be avoided, but exposure to ambient moisture cannot be avoided. Perovskite can be hydrated by water molecules to form a monohydrate phase [4,5]. By comparing XRD patterns after and before exposed to water, scientists postulated the following moisture-catalyzed breakdown process of the perovskite layer:



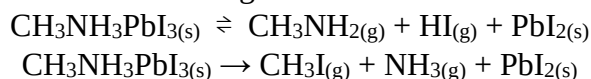
A 4-step breakdown mechanism for $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite absorber degraded into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 following interaction with oxygen and moisture, which can be seen that the color shift from darkish brown to brilliant yellow. It degrades into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 first, and produces HI aqueous solution, PbI_2 solid, and volatile CH_3NH_2 afterward [6].



Dihydrate formation is also conceivable in films [6,7]. Both reactions can be reversed. If hydrated materials are maintained in moisture-free or an inert environment, due to phase segregation, they could be dehydrated to generate perovskite with a small degree of irreversibility. The perovskite hydration promotes deformation of $(\text{PbI}_6)^{4-}$ octahedra structure and converts their 3D network into a 1D octahedra chain for monohydrates, also 0D for dihydrates. Those factors moderate the chemical bonding between the $(\text{PbI}_6)^{4-}$ and the A-site moiety, which perovskites are more susceptible to external effects like electric bias and heat. Once the perovskite is saturated with water, the hydration will become irreversible, and the material will dissolve irreversibly into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$. Due to the hydrophilic character of the material, it quickly absorbs water from its surroundings, leading to the creation of hydrate-like substances $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ [7].

3.2. Thermal effect

The fluctuation in temperature causes structural instability in the perovskite material. MAPbI_3 can be decomposed at 85°C in an environment devoid of oxygen and moisture, often known as an inert atmosphere. Compare unheated perovskites with nano-electrical properties to heated perovskites, a direct indication of this fact has been observed [8,9]. Later, the suggested reversible and irreversible processes of perovskite breakdown via heating are discussed.



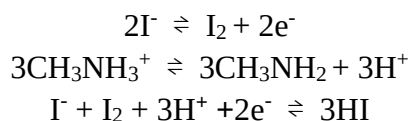
Generally, at ambient temperature, the MAPbI_3 occurs in a tetragonal structure. At elevated temperature, more symmetry appears, and structure of the crystal displays a cubic phase (tolerance factor (t)= 0.9-1.0), whereas at lower temperatures, symmetry decreases, and the crystal structure displays an orthorhombic phase (tolerance factor (t)= 0.7-0.9). Due to the lattice distortion, the performance of MAPbI_3 -based PSCs is negatively impacted.

Other components are required for PSCs. A slightly greater temperature can also degrade these compounds. Spiro-OMeTAD is frequently used in n-i-p PSCs hole transporting. At 100°C , it crystallized, decreasing the efficiency of solar cells. And hole-transporting layers (HTLs) along with additives can evaporate at temperatures below 85°C [10]. Attempts are made to substitute organic charge-transporting layers with oxides, however heating electron-transporting oxides such as ZnO to 100 degrees Celsius damages the perovskite [8,9].

3.3. Illumination effect

Light harvesters are essential in determining the total stability. By implementing certain tactics, influences of factors like as oxygen, moisture, and heat can be decreased or eliminated. Nonetheless, solar illumination is unavoidable, as all solar cells require lighting and electrical bias to generate electricity. As indicated previously, although numerous alterations are made to the transport layer of

PSC devices, TiO_2 is commonly placed as the ETL, which is susceptible to degradation under UV irradiation. The deterioration mechanism under UV irradiation is described by the following equations:



The TiO_2 layer removes an electron which destroys the perovskite structure, resulting in the I_2 creation [10]. However, when exposed to ultraviolet light, the desorbed oxygen from the deep trap and oxygen vacancy sites is activated, which promotes charge carrier combination and, thus, affects device performance by decreasing FF and V_{oc} [9].

According to multiple publications [11,12], even after a few hundreds of hours of exposure to light, MAPbI_3 does not degrade, as evidenced by absorption. The ionic conductivity enhanced by visible light irradiation through many orders of magnitude [12], and these photoinduced changes can be helpful for PV properties in perovskite. Light-induced perovskite lattice expansion increases the device's power conversion efficiency (PCE).

4. Strategies for Preventing Degradation and Improving Stability

Numerous PSC degradation mechanisms are explored in the first part. These degradations can be lessened by implement diverse strategies, result in stability improvement, and effectiveness preservation. Some strategies target a single degradation path, whereas others claim multipronged approaches in which a single strategy can aid in fighting numerous types of degradation.

4.1. Stability induced by the charge-transport layer

The effect of charge-transporting layer on the stability and performance of PSCs is substantial. In this context, the charge transport layer's electrical band structure is somehow crucial. The energy levels must be appropriately aligned to enable the efficient transfer of photogenerated charge to the respective electrodes, for example, HOMO-LUMO in the organic compound and valence band conduction in inorganic semiconductor species. The energy levels are well-balanced could allow charge separation and reduction in recombination. Such parts would enhance the short-circuit current density and fill factor. The critical factor of charge transport layer's performance is the charge carriers (electrons or holes) mobility, where charge transfer is expedited by a greater mobility. If two charge-transporting materials with varies mobilities and the same charge carriers' concentration, the material have greater mobility shows superior conductivity. More efficient charge transport layer decreases energy loss and increases open circuit voltage, so stable charge-transporting materials are needed. The stability of charge-transporting layers can be significantly enhanced by two-side diffusion engineering, an inward diffusion from external factors and an outward diffusion of iodine from the perovskite layer, which allows sufficient thickness [12-14].

4.2. Electron-transport layer

For electron-transport layer of PSCs, several metal oxides (both binary and ternary) have indeed been employed. The valence and conduction bands of MAPbI_3 have energies of -5.4 eV and -3.9 eV, respectively. To accept photogenerated electrons from the perovskite, the edge of valence band must be significantly under -5.4 eV to prevent photogenerated holes, whereas the edge of conduction band of the ETL material must be at or under -3.9 eV [12]. The mesoporous TiO_2 layer was selected as ETL material because it was the most suited material for a solar cell with a sensitized junction [15]. As ETL for PSCs, several nanostructures of TiO_2 have been used [12]. Some of them, such as nanodendrite structures with branching that decrease the length of electron diffusion and boost trapping of light, have been demonstrated to be favorable. Snaith and his group have substituted PSCs with a substantially thinner mesoporous TiO_2 layer, yielding an effective planar device [16]. These

reduced combination pathways between HTL and ETL boosts efficiency from 2.6% to 8.2%. However, the most significant issue with TiO_2 is that it can be damaged by sun UV radiation.

ZnO is regarded a good contender for ETL due to its greater electron mobility than TiO_2 . However, ZnO ETL has various challenges, including poor perovskite wetting and perovskite deterioration. Perovskite degrades at the ZnO interface because radicals such as the hydroxyl ($-\text{OH}$) group are present [17]. This problem has been addressed from two angles: 1). To introduce an extra layer between ZnO and perovskite with the correct energy level alignment, the ZnO - CdS core-shell structure is utilized as ETL, where CdS lies between perovskite and ZnO interface [18]. The correct CdS band alignment facilitates photogenerated electron flow from perovskite to ZnO interface. This method can be last for at least two months [18]. 2). High-vacuum methods for physical deposition of ZnO , the pulse laser deposition (PLD) has been demonstrated successful in producing efficient and stable devices [19]. The physically generated ZnO films surface is lack of chemical groups responsible for perovskite breakdown, such as the hydroxyl group. Consequently, they can provide high levels of stability and efficiency.

4.3. Hole transport layer

Carbon-based HTL materials form stable PSCs due to their thermal and chemical stability. Moreover, the electronic band structure, Fermi levels, and high conductivity of carbon-based material make them appropriate for use as HTL and electrode materials simultaneously, with better and flexible function, and cheaper manufacturing cost [19]. In addition to being suitable for a wide range of applications, single wall carbon nanotubes may be combined with other HTL types to improve their properties [20].

Organic HTLs are reported widely in the research on PSCs, can be split into two categories: 1) molecules with small size and 2) Spiro-OMeTAD polymers and isomers are the most prevalent. First, Lithium is a small “sized” molecule, the low hole mobility values require the use of Li-salts to increase hole mobility. However, Li-salts may be susceptible to water absorption, which can be damaging to their stability [20]. Then, due to the advantageous shifting of electronic states, fluorinated analogues of Spiro-OMeTAD are hydrophilic and very efficiency hole-transport materials. The constitutional isomerism of Spiro-OMeTAD polymers have been studied experimentally, atomistically, and theoretically, and PSCs fabrication techniques achieved excellent efficiency of 24.82% (certificated at 24.64% with 0.3-volt voltage deficit) and more stable in humid environments without encapsulation (retented 87% efficiency after 500h) [21].

4.4. Encapsulation

Encapsulation, or packaging the device with suitable materials, is one of the most successful methods to enhance the PSCs stability. Encapsulation can withstand extrinsic influences that cause PSCs to degrade. Effective encapsulation must prevent the infiltration of outside moisture and oxygen inside the perovskite layer; protect leakage of volatile organic solvents from the device; endure mechanical stress during the device's thermal fluctuations; also impervious to mechanical forces such as moisture, snow, and hail [14]. If the encapsulation is also located on the topside, facing the light, for instance, it may be readily cleaned and transparent enough to enable adequate light to reach the actual device [22]. Water vapor transmission rate (WVTR) can be used to measure the efficiency of an encapsulating material [22]. Perovskite moisture instability is identified early on, and a multilayer inorganic/organic film containing Al_2O_3 is utilized for encapsulation [23]. Different aspects of encapsulation using epoxy resin are examined. Cross-linked grain encapsulation improves perovskite's moisture endurance and defect passivation simultaneously, data shows encapsulated perovskite with bandgap of 1.55 eV exhibited a PCE value of 22.7%, and over 90% of the starting PCE was maintained after 10,000 hours of shelf storage at room temperature [23].

Recent research has demonstrated that tri-iodide PSCs require nano-structured TiO_2 scaffold because it enhances the effective electron diffusion length and wraps the titania layer surface to prevent UV irradiation from exposing it. Europium (Eu^{3+}), a rare earth (RE) element doped with

yttrium Vanadate (YVO_4) to form $\text{YVO}_4\text{:Eu}^{3+}$, shows great ability to resist UV degradation of PSC devices. Because RE elements have 4f orbitals and specific electro-, photo- and magneto-properties [24]. Transparent coating is sprayed by downshifting (DS) nanoparticles, which enables absorption of ultraviolet (UV) radiation and reduction of UV degradation. The downshifting PSC have greater PCE due to the downshifting of UV light into the visible spectrum and enhanced path-length of long-wavelength light caused by scattering. To enhancing the UV stability and photocurrent of PSCs would need a wider absorption band DS material, able to absorb 300–400 nm portion in UV spectrum efficiently [24].

5. Conclusion

The efficiency of PSCs for laboratory-scale devices shortly topped 25.7%. However, quick stabilization is required for commercialization. In practice, commercialization necessitates the concurrent development of high-efficiency, large-area, and long-lasting devices. To prevent deterioration, it is essential to know its fundamental mechanisms. At now, not all degradation processes are fully understood, despite the fact that there is a race to enhance the power conversion efficiency (PCE) of perovskite solar cells (PSCs). More study is necessary to acquire a deeper understanding of the degradation mechanisms generated by diverse factors, then to improve the stability and efficiency of PSCs in further aspect.

Several strategies are utilized to counteract instabilities. Numerous methods have been shown to be multifunctional. For instance, a single method or material addition can improve numerous parameters. Encapsulation is a crucial aspect for commercialization in the context of current trends. The majority of PSCs satisfied the IEC standards in full or in part, and they all utilized unique encapsulation techniques. Various aspects of a device may contribute to its instability; therefore, a multifaceted strategy may be necessary to concurrently address these causes and build a stable, high-performance device. Even as the PSCs have attained adequate efficiency and the higher efficiency levels are undergoing rapid improvement, operational stability should be prioritized. A standardized method for assessing operational stability has indeed been developed. Each newly produced device must subject to the suggested stability testing standard. The global PSCs research community is large-scaled, and published information increases each day. Urgently necessary are the establishment of a database, personalization, and acceptance of standard testing methodologies.

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