

MINI-REVIEW ON THE STABILITY OF PEROVSKITE SOLAR CELLS

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Abstract

Perovskite solar cells (PSCs) are an emerging photovoltaic technology which is quickly approaching the performance of silicon solar cells. This promising technology opens the possibility for new applications like flexible and semi-transparent solar cells that could be used in windows and green houses. The addition of perovskites to current commercial panels cells is also regarded as a way to boost the current solar energy harvesting capacity. Due to degradation of the perovskite materials, PSCs device have shown limited operating life time. So in this review we have presented the most recent research on understanding of the factors that may cause the degradation process in perovskitematerials and PSC devices.

I. Introduction

Over last few decades, the massive exploitation and consumption of natural resources have created major problems to the human development due to the energy deficiency and environmental pollution. The innovation of photovoltaic (PV) technology has made a series of clean and renewable energy resources to elucidate energy and environmental problems. For instance, the demand for electricity all over the worldwide is growing rapidly, and is likely to triple by 2050¹. Hence, if the goal of 80% renewable electricity by 2050 is to be achieved, it is imperative that PVs play a major role in the future of electricity generation in the world.

The PV effect for the first time was observed by Becquerel in 1839. He used thin silicon wafers to transform sunlight energy into electrical power. The next major advance was made in 1940, the first modern solar cell made of silicon was invented by Russell Shoemaker Ohl. Later, in April, 1954, researchers at Bell Laboratories demonstrated the first practical silicon solar cell². This works on the principle of electron-hole creation in each cell composed of two different layers (p-type and n-type materials) of a semiconductor material, as shown in **Figure 1**. Light travels in packets of energy called photons. The generation of electric current happens inside the depletion zone of the PN junction. The depletion region is the area around the PN junction where the electrons from the N-type silicon, have diffused into the holes of the P-type material. When a photon of light is absorbed by one of these atoms in the N-type silicon it will free an electron, creating a free electron and a hole. The free electron and hole has sufficient energy to jump out of the depletion zone. If a wire is connected from the cathode (N-type silicon) to the anode (P-type silicon) electrons will flow through the wire.

The electron is attracted to the positive charge of the P-type material and travels through the external load (meter) creating a flow of electric current. The hole created by the dislodged electron is attracted to the negative charge of N-type material and migrates to the back electrical contact. As the electron enters the P-type silicon from the back electrical contact it combines with the hole restoring the electrical neutrality.

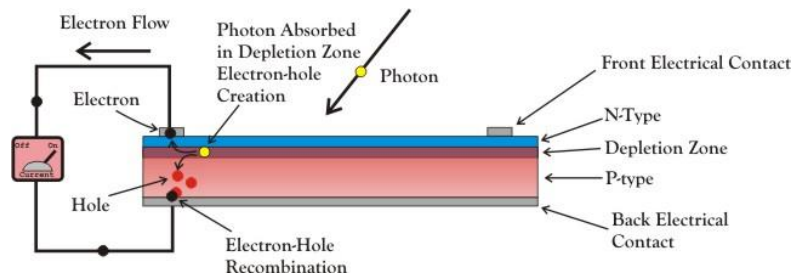


Figure 1. Schematic representation of a solar cell, showing the n-type and p-type layers.

The PV solar cells are made-up of different materials, such as, silicon (single crystal, multi-crystalline, amorphous silicon), cadmium-telluride, copper-indium-gallium-selenide, and copper-indium-gallium-sulphide³. Based on these materials, the PV solar cells are characterised into different classes as shown in **Figure 2**. **Figure 3** shows the data taken from NREL solar cell efficiency tables, demonstrated that the photon conversion efficiencies (PCE) of the perovskite based devices improved more and more recent years in comparison to other technologies⁴. This suggests that with continued research, efficiency of perovskite based solar cells can continue to rise at this rate over the coming years.

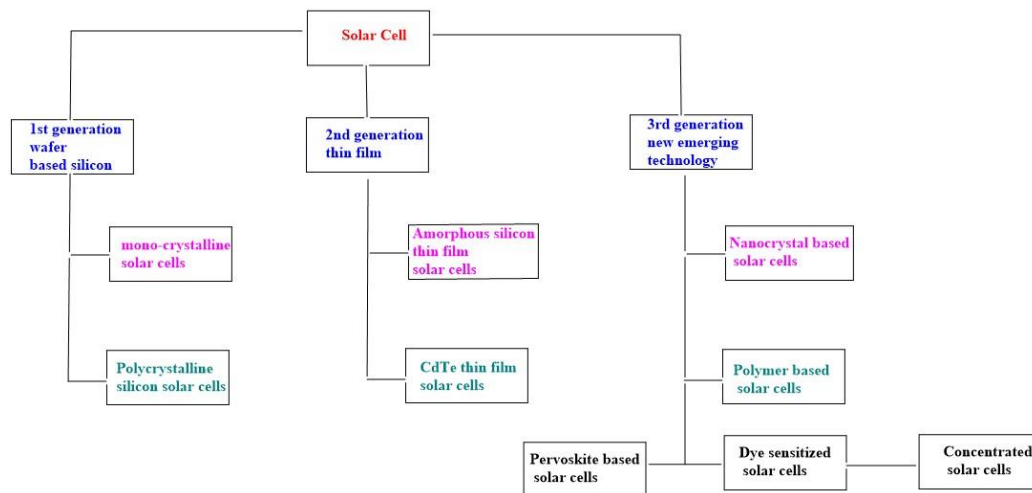


Figure 2. Different types of solar cells

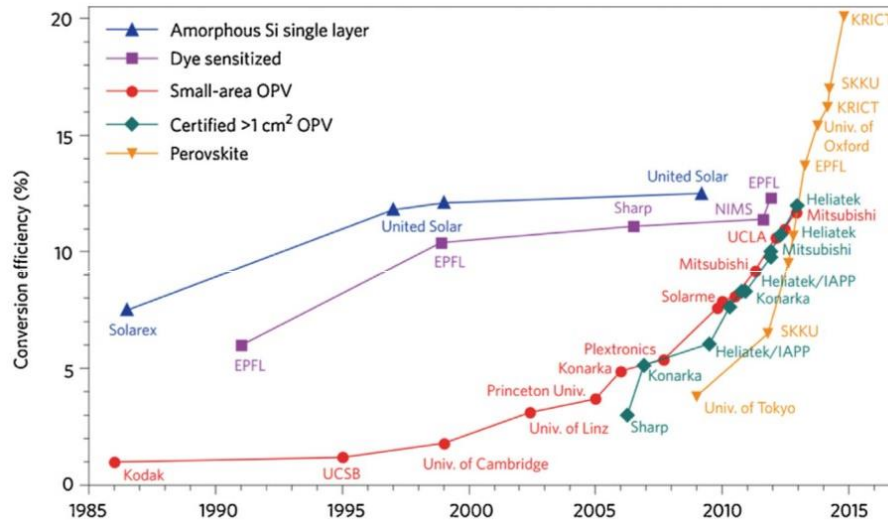


Figure 3. Perovskite solar cells have increased in power conversion efficiency at a phenomenal rate compared to other types of photovoltaics.

II. Perovskite solar cells

Perovskite structure

Perovskites derive their name from the mineral structure of calcium titanium oxide (CaTiO_3), discovered by German mineralogist Gustav Rose in the year 1839. This structure was later characterized by Russian mineralogist Lev A. Perovski, from which it derives its name. A perovskite is a large family of materials with the generic formula ABX_3 , where A and B cations have 12 and 6 coordinates with X anions, respectively⁵. The crystal structure of a perovskite is shown in Figure 4, which contains a large atomic or molecular cation (positively charged) of type A in the centre of a cube. The corners of the cube are occupied by atoms B (also positively charged cations) and the faces of the cube are occupied by a smaller atom X with negative charge (anion).

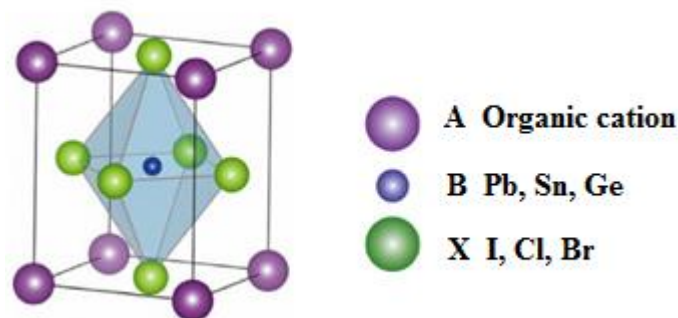


Figure 4. A generic perovskite crystal structure of the form ABX_3 .

Size of A and B ions greatly influences the structure of perovskite crystal lattice, and their radii correlation is expressed through tolerance factor (eq 1)

$$t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)} \dots\dots\dots(1)$$

The cubic phase is stabilized when $(R_A + R_X) = 2^{1/2}(R_B + R_X)$, where R_A , R_B , R_X are the ionic radii of A, B, X, respectively. Ideal cubic structure occurs when $t = 1$, while $t < 1$ indicates that A is too small and $t > 1$ means A is too large to fit in the cavity between BX_6 octahedrons. To further compliment Goldschmidt's tolerance factor in constructing a structure map for perovskites, an octahedral factor (μ) was developed by Li and company. It provides a ratio of the ionic radii of the B cation to the X anion, given $\mu = R_B/R_X$, that is directly correlated to the BX_6 octahedron. According to this factor, halide perovskite formation occurs for $\mu > 0.442$, whereas below this value BX_6 octahedron will become unstable and a perovskite structure will not form. So far the most efficient perovskite solar cells devices based on methylammonium lead halides, $CH_3NH_3PbX_3$ ($X = Cl, Br, I$), has been investigated due to their better optoelectronic properties.

Recent progress in efficient hybrid lead halide perovskite solar cells

The first appearance of the organic cation, methylammonium (MA), in halide perovskites was seen by Weber and Naturforsch in 1978 for I, Cl, and Br. In 1994, Mitzi et al was used the two-dimensional perovskites that featured strong excitonic characteristics and demonstrated applications in thin-film field effect transistors.⁶ In 2009, Miyasaka et al⁷ investigated $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ as a light absorbing layer in liquid based dye sensitized solar cells with the device structure shown in Figure 5(a). A power conversion efficiency of 3.1 and 3.8% were achieved. In 2011, Park et al⁸ improved the efficiency of $CH_3NH_3PbI_3$ sensitized solar cells to 6.5% by employing perovskite nanoparticles (~2.5 nm in diameter) on TiO_2 to serve as sensitizers for improved absorption over conventional dyes. The major drawback of the perovskite-sensitized liquid-type DSSC was the instability of the deposited $CH_3NH_3PbI_3$ in liquid electrolyte. This can be solved by replacing liquid electrolyte with solid hole conductor spiro-MeOTAD.

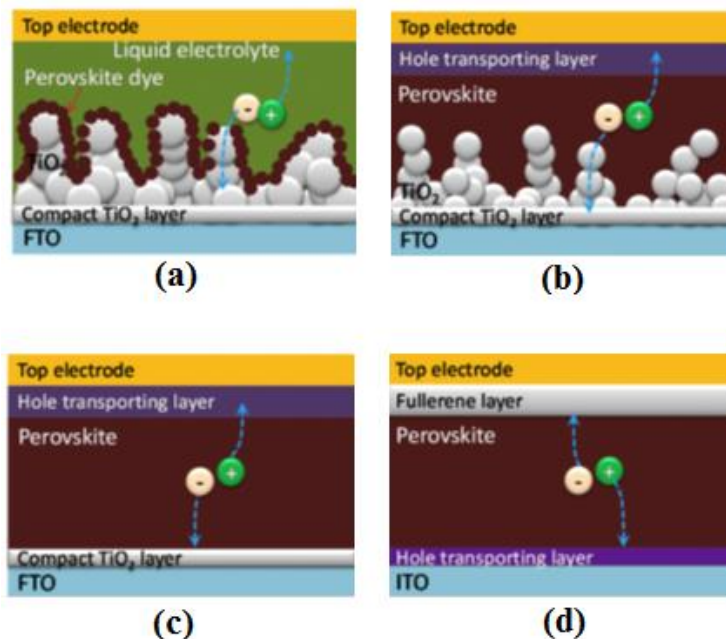


Figure 5. (a) Liquid DSSC structure perovskite solar cells with mesoporous TiO_2 layer and liquid electrolyte where the perovskite material worked as a sensitizer. (b) Solid-state DSSC structure perovskite solar cells with mesoscopic TiO_2 layer. (c) N-i-p planar heterostructure perovskite solar cells with a compact TiO_2 layer. (d) P-i-n planar heterostructure perovskite solar cells with a flat hole transporting layer at the bottom and fullerene transporting layers at the top.

In 2012, N. G. Park and his colleagues⁹ has achieved an efficiency as high as 9.7% together with excellent stability by using a solid 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD) as a hole transport layer and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an absorbing layer deposited on an electron transporting thin TiO_2 layer ($\sim 0.6 \mu\text{m}$) (see **Figure 5(b)**). The device demonstrated 500 h-stability in air at room temperature, which was achieved without encapsulation. The two research groups performed experiment in 2013, which attracted a broad interest from photovoltaic society. Gratzel et al.¹⁰ reported that a two-step sequential deposition process, first PbI_2 spin coating deposited on mesoporous TiO_2 layer and then dipped in a solution containing $\text{CH}_3\text{NH}_3\text{I}$, forming a high quality perovskite absorbing layer in the solid-state DSSC devices (shown in **Figure 5 (c)**), can yield device efficiency close to 15%. Snaith et al.¹¹ also demonstrated a high efficiency of 15% but in planar heterojunction structure solar cells where the mesoporous TiO_2 layer was replaced with only a compact TiO_2 layer (**Figure 5 (d)**). These reports shown the ambipolar nature of perovskites, which enlightened and encouraged the intensive employment of the planar hetero junction architecture in these devices.¹²⁻¹³ Meanwhile, Kim and co-workers⁹ reported a mixed-halide perovskite by using chlorine-containing pre-cursors, demonstrating improved carrier transport, diffusion lengths and stability over its triiodide counterpart. Later, bromine inclusion was reported to feature an adjustable band gap for perovskites.¹⁴ A PCE close to 20% has been achieved in both mesoporous structure devices as well as PHJ devices recently. This sparked a massive progress in the hybrid lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Cl}, \text{Br}$), obtaining a record PCE reaching up to 20.1% in just five years using low cost production methods compared to other perovskite materials (see **Figure 6**).

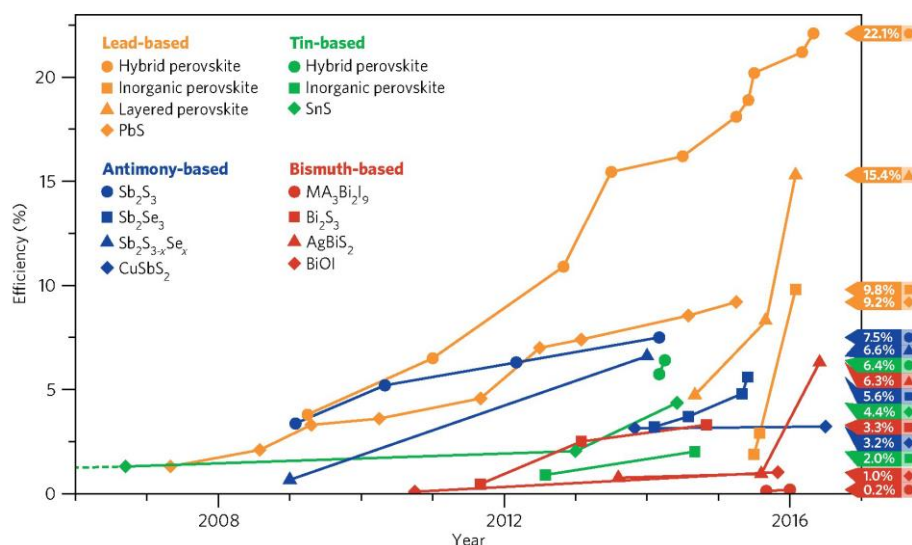


Figure 6. Efficiency improvements over time for perovskite solar absorbers.

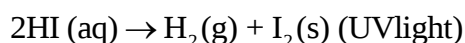
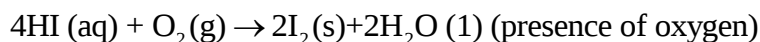
Although the remarkable recent achievements reported for perovskite-based solar cells, many basic material properties including charge transport and recombination processes are not yet clearly understood on a fundamental level for this type of materials. On the other hand, a perovskite solar cell also faces some major challenges, such as, material toxicity, device hysteresis, and long term stability of perovskite material, in achieving its high potential.

III. Factors influencing the stability of perovskite materials

The stability of perovskite solar cells associated with the stability of perovskite materials itself and the stability of solar cell devices. The stability of perovskite materials is impact by the various degradation process such as (a) the interaction of water molecule with perovskite materials (b) the migration of electrode metal through the hole transfer materials (HTM) to interact with perovskite film (c) the different halide composition in the perovskite compound (c) the decomposition of perovskite material induced by UV light exposure (d) oxygen and temperature.

i. Impact of moisture and oxygen

The existence of hygroscopic amine component in perovskite materials causes the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of oxygen and moisture. For instance, once $\text{CH}_3\text{NH}_3\text{PbI}_3$ is exposed to water molecule, the chemical stability of this compound is represented by several chemical reactions as given below¹⁵



Several researchers thought that the water is major degradation source for perovskite solar cells. Even though the mechanism is not fully understood, but it is clear that hybrid perovskites can react with Lewis bases such as water to irreversibly release $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . The possible process of $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposition was displayed schematically by Frost et al.¹⁶ The irreversible degradation of the perovskite layer is a problem for the lifetime of photovoltaic cells. On the other hand, the PbI_2 , itself, is soluble in water and cause significant eco-toxicological problems in the field. Furthermore, keeping complete device under ambient condition has also been found to cause degradation of perovskite materials due to the impact of humidity. It is reported that humidity of 55% or above will lead to a significant decrease of the performance of solar cells with $\text{CH}_3\text{NH}_3\text{PbI}_3$ due to the degradation of the light absorbing materials.¹⁴ Christians et al.¹⁷ have investigated the interaction between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and H_2O vapour in dark by monitoring the morphology, crystal structure and optical absorption properties of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films in the presence of 0%, 25%, 50% and 90% relative humidity (RH) at room temperature in the dark. Their results have shown that there was a complex interaction in this system, resulting in the formation of $(\text{CH}_3\text{NH}_3)_4\text{Pb}_2\text{H}_2\text{O}$. This caused a change in the crystal structure of perovskite materials, leading to decrease in the light absorption ability of the material over the visible spectral region.

ii. Impact of perovskite composition

Recently, Noh et al.¹⁴ and Misra et al.¹⁸ have investigated the degradation of $\text{CH}_3\text{NH}_3\text{PbX}_3$ films ($\text{X} = \text{I}$ or Br) under concentrated sunlight of 100 suns. Their studies indicate that the degradation processes is strongly dependent on the composition of perovskite materials. They also suggest that the degradation process is depends on the light intensity and temperature. For instant, $\text{CH}_3\text{NH}_3\text{PbI}_3$ degraded after exposure to 100 sun lights at sample temperature $\sim 45\text{--}55^\circ\text{C}$. But, no degradation in the material was observed after exposure to the same sunlight concentration at a lower temperature of $\sim 25^\circ\text{C}$. Whereas, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ did not decompose after exposure to similar light intensity and temperatures, suggesting the better stability of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films compared with its iodide counterpart. So far solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ ($x = 0.2$) exhibited better stability at high humidity ($>50\%$) than the device with $\text{CH}_3\text{NH}_3\text{PbI}_3$. The cell performance remained unchanged at low humidity ($<50\%$ RH) within 20 days.

iii. Impact of annealing temperature

Due to the impact of annealing temperature on the stability and photovoltaic performance of devices, mostly, low temperature annealing is used during fabrication process of perovskite thin films for solar cells. Recent studies^{19,20} report that a minimum temperature of 80°C is required to completely transform the precursor of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 to $\text{CH}_3\text{NH}_3\text{PbI}_3$. However, further increase of the annealing temperature would lead to the change of the perovskite morphology and formation of larger crystalline particles on the surface of mesoporous TiO_2 film substrate. This causes the variation in electronic and optical properties of perovskite material.

iv. Influence of UV light

In 2015, the photodecomposition of the binary lead halides has investigated by Schoonman.²¹ He suggested that upon UV light irradiation for short irradiation time in PbX_2 causes formation of metallic lead. Similarly like lead halides, if $\text{CH}_3\text{NH}_3\text{PbX}_3$ exhibits photodecomposition under UV irradiation, then this will be an extra factor for instability of PSCs. Wei et al.²² reported that the photo stability is effect by the chemical composition of the organic and inorganic part and spatial arrangement in the crystal structure of Perovskite material. Therefore, it is important to investigate the dynamic behaviour of the photo-generated charge carriers in $\text{CH}_3\text{NH}_3\text{PbX}_3$ and trapping of the photoelectrons at lead ions.

IV. Factors influencing stability of perovskite solar cell device

The basic device structure of the perovskite solar cells is shown in Figure 7. Which contains the which consists of FTO substrate, TiO_2 compact (c- TiO_2) layer, mesoporous TiO_2 (m- TiO_2) layer, organometalperovskite materials, hole trasport materials (HTM) and back electrode contact. Generally, the stability of the PSC device is influence by the different fabrication methods, mesoporous metal oxides and HTM.

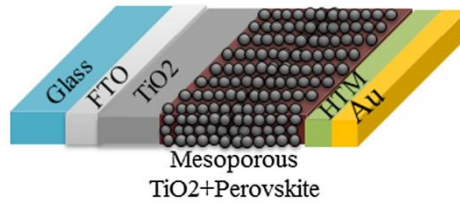


Figure 7. A schematic illustration of perovskite device structure

i. Effect of fabrication method

The PSC device is fabricated with different methods such as blade coating, spin coating, two step deposition, one step – spin coated inside glove box and hybrid chemical vapour deposition, alternating layer-by-layer vacuum deposition. Among these methods hybrid chemical vapour deposition and alternating layer-by-layer vacuum deposition methods shown to be favourable for higher photovoltaic efficiency. For instant, in 2014 Leyden et al.²³ reported that the perovskite cells made by hybrid chemical vapour deposition method exhibited high efficiency of 11.8% and demonstrated the same efficiency after 1100 h storage in dark and dry N₂ gas. In contrast, the device fabricated with the alternating layer-by-layer vacuum deposition method evoked 91% of its initial value after 62 days' storage under ambient conditions. This superior stability is due to the formation of dense perovskite film with full surface coverage that prevents moisture penetration.

ii. Effect of the structure of metal oxide film

The most commonly used mesoscopic metal oxides are usually composed of either TiO₂ or Al₂O₃ (although Al₂O₃ only provides a mesoscopic support, and does not transport electrons), and n- type metal oxides such as ZnO and TiO₂ are commonly used as compact electron transporting layers in planar perovskite devices. Some evidence suggests that the use of mesoporous TiO₂ or mesoporous Al₂O₃ layers results in improved stability for perovskite- based solar cells. Recently, Fakharuddin et al.²⁴ have compared the long term performance of PSC using three different TiO₂ film structure (a planar device with TiO₂ compact layer; a device with TiO₂ rutile nano-rod and a device with TiO₂ nano-rods post treated with TiCl₄ solution) and found that the different stability of the PSC devices was related to the crystallinity and chemical stability of the scaffold layer.

iii. Effect of different hole transport materials (HTM)

Generally, it is assumed that perovskite material is protecting from atmosphere moisture by placing a HTM layer above it. But, literature showed that the mostly used HTM such as spiro-OMeTAD is sensitive to moisture. This indicates that the stability of the perovskite solar cells is depends on the hydrophobicity and density of the HTM. So in order to enhance the stability of the PSC devices, Christians et al.¹⁷ is replaced spiro-OMeTAD with inorganic CuI. They found that better stability of the device when compared to cells with spiro-OMeTAD upon continuous 2h illumination. But long term stability of the devices was not reported in their work. Literature shows the similar studies by considering different HTMs. **Figure8** shows the temperature dependence of power conversion efficiency for

perovskite solar cells employing different hole transport materials. The device with Li-TFSI doped Spiro-OMeTAD, P3HT and PTAA suffer a significant decrease in efficiency after being heated to 100 °C and no recovery was observed after cooling of these devices.²⁵

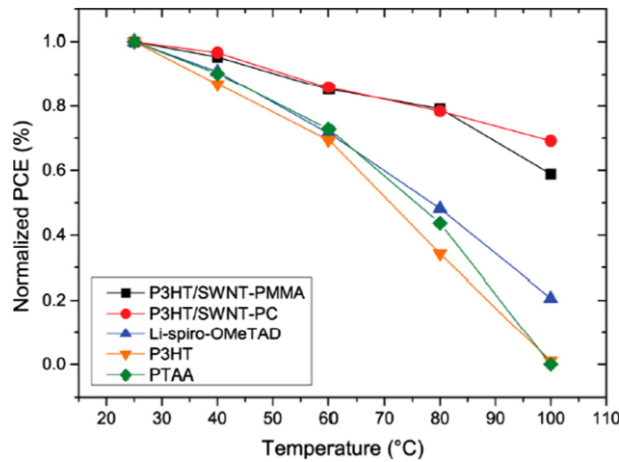


Figure8. Temperature dependence of efficiency for provskite solar cells using different hole transport layers.

V. Conclusions

In summary, despite the fact that PSCs have exposed notable efficiency with silicon solar cells, both perovskite material and solar cell devices need to overcome the stability issues associated with practical applications. Therefore, in order to develop effective strategies to resolve stability issue, it is essential to have in-depth knowledge of the physicochemical processes involved in the degradation of the perovskite materials. This involves a broad study of the perovskite materials and solar cell devices using experimental techniques combined with theoretical modelling. Another major issue in this area is the difficulty in direct comparison of the results of stability testing from different groups due to the different experimental conditions. In future, it is crucial and essential to standardize and control of experimental conditions is required in order to enable easy replication of results across different laboratories. From material point of view, it is necessary to develop new perovskite material which has robust stability without phase transitions or decomposition at device operational conditions.

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