

Review

Encapsulation of Organic and Perovskite Solar Cells: A Review

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Abstract: Photovoltaic is one of the promising renewable sources of power to meet the future challenge of energy need. Organic and perovskite thin film solar cells are an emerging cost-effective photovoltaic technology because of low-cost manufacturing processing and their light weight. The main barrier of commercial use of organic and perovskite solar cells is the poor stability of devices. Encapsulation of these photovoltaic devices is one of the best ways to address this stability issue and enhance the device lifetime by employing materials and structures that possess high barrier performance for oxygen and moisture. The aim of this review paper is to find different encapsulation materials and techniques for perovskite and organic solar cells according to the present understanding of reliability issues. It discusses the available encapsulate materials and their utility in limiting chemicals, such as water vapour and oxygen penetration. It also covers the mechanisms of mechanical degradation within the individual layers and solar cell as a whole, and possible obstacles to their application in both organic and perovskite solar cells. The contemporary understanding of these degradation mechanisms, their interplay, and their initiating factors (both internal and external) are also discussed.

Keywords: organic solar cells; perovskite solar cells; encapsulation; stability

1. Introduction

Organic photovoltaic (OPV) and Perovskite solar cell (PSC) are promising emerging photovoltaics thin film technology. Light harvester metal-halide perovskite materials, such as methyl-ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), have exhibited small exciton binding energy, high optical cross-section, superior ambipolar charge transport, tuneable band gaps, and low-cost fabrication [1]. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSCs and OPV devices can be solution-processed, which is suitable for roll-to-roll manufacturing processes for inexpensive largescale commercialization. The power conversion efficiency (PCE) of OPV devices have overpassed 14% for single junction and 17% for tandem devices to date with the development of low band-gap organic materials and device processing technology [2–5]. The achievement of the highest PCE of PSCs over 23.3% has shown promising future directions for using in large-scale production, together with traditional silicon solar cells [6]. Low-temperature ($<150\text{ }^\circ\text{C}$) and solution-processed ZnO based electron transport layer (ETL) is one of the most promising materials for large scale roll-to-roll fabrication of perovskite and organic solar cells, owing to its almost identical electron affinity (4.2 eV) of TiO_2 . Arafat et al. have already demonstrated aluminium (Al) doped ZnO (AZO) ETL of PSC with cell efficiency over 18% [7]. Currently, the poor stability of OPV and perovskite solar cells is a barrier for the commercialisation [8]. It is believed that oxygen and moisture are the external main reason for degradation of organic and PSCs, as shown in Figure 1 [9]. All the internal possible degradation mechanisms in PSCs can be controlled by careful interface engineering, such as a good choice of cathode and anode interlayer materials, ion-hybridizations in perovskite layer, etc.

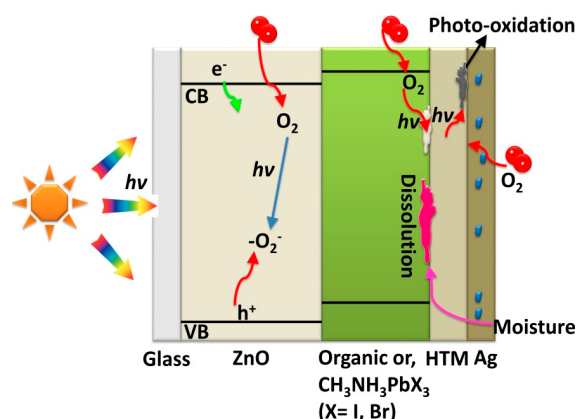


Figure 1. Schematic diagram of an organic/Perovskite solar cell (PSC) solar cell structure. The electron-hole pair recombination, moisture dissolution of perovskite material and photo-oxidation processes at the interface between hole transport materials (HTM) and metal electrode are shown. Adapted with permission from [9]. Copyright 2018 Royal Society of Chemistry.

Encapsulation of organic and perovskite solar cells can play an effective role in improving the stability of both devices. The encapsulation layer can act as a barrier layer by restricting the diffusion of oxygen and moisture through this encapsulation material, resulting in the protection of the cathode interface and the active layer from deterioration as shown in Figure 2. Encapsulation materials should have high barrier performance for oxygen and moisture. The encapsulation material layer structure is a critical factor to overcome these issues and enhance the device stability [10].

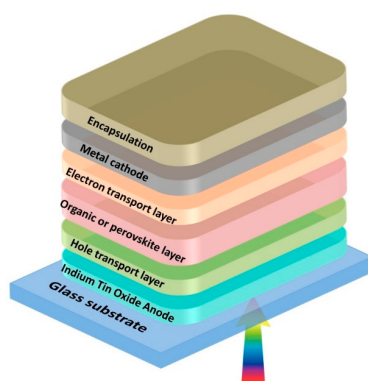


Figure 2. A schematic diagram of an organic or perovskite solar cells structure with an encapsulation layer.

The encapsulation material needs to possess good process ability, low water absorptivity, and permeability. Encapsulation materials should have relatively higher dielectric constant, light transmission, and resistance to ultraviolet (UV) degradation and thermal oxidation. They also require excellent chemical inertness, adhesion, and mechanical strength [11,12]. Oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) are the steady state rates at which oxygen and water vapour gas can penetrate through a film that affects the encapsulation layer. A schematic diagram of organic and/or perovskite solar cells device is shown in Figure 2 with an encapsulation layer. This encapsulation layer material should have the following (Table 1) required properties to protect the device from the oxygen and water vapour effects. A list of specifications of requirements of encapsulation materials is listed in Table 1.

Table 1. Specifications and requirements for encapsulating materials for the protection of organic and perovskite devices from the oxygen and moisture. Reprinted with permission from [12]. Copyright 2016 John Wiley & Sons, Inc.

Characteristics	Specification of Requirement
WVTR	10^{-3} – 10^{-6} g·m ⁻² ·day ⁻¹
OTR	10^{-3} – 10^{-5} cm ³ ·m ⁻² ·day ⁻¹ ·atm ⁻¹
Glass transition temperature (T_g)	<−40 °C (during the winter in deserts)
Total light transmission	>90% of incident light
Water absorption	<0.5 wt % (20 °C/100% RH)
Tensile modulus	<20.7 mPa (>3000 psi) at 25 °C
UV absorption degradation	None (>350 nm)
Hydrolysis	None (80 °C, 100% RH)

To determine the value of OTR, it is necessary to use a colorimetric sensor [13,14]. The OTR was calculated by measuring the amount of oxygen during a certain period at a constant rate that it passed through the cathode. By knowing the value of OTR and WVTR it is possible to determine how good is the encapsulated materials performance for the protection of perovskite and OPVs devices from degradation through their lifetime and performance. The effective WVTR can be determined by monitoring the temporal rate of change of the cathode (metal) electrical conductance. If it is assumed that the diffusivity of water vapour and oxygen obeys Fick's law (diffusivity is independent of concentration), then the WVTR or OTR can be described as [15]:

$$\text{WVTR}(t) = \frac{DC_s}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{\frac{-Dn^2\pi^2 t}{l^2}} \right] \quad (1)$$

where D is the diffusivity, C_s is the surface saturation concentrations, t is the time, and l is the film thickness. Normally, D increases with increasing temperature. WVTR and OTR is also a function of temperature.

The good performance encapsulation materials should have a value larger than 10^{-6} g·m⁻²·day⁻¹ for WVTR (Table 1) to protect the OPV and PSCs devices [16]. As an example, an OPV device with a structure ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Al was encapsulated using ZnO and UV resin with a large WVTR value of 5.0×10^{-1} g·m⁻²·day⁻¹ [17]. In Ref. [18], the WVTR value was found as big as of 100 g·m⁻²·day⁻¹ for an encapsulated OPV (ITO/PEDOT:PSS/P3HT:PC₇₁BM/Ca/Al) with an epoxy resin. On the other hand, in Ref. [17] OPVs cells under the configuration ITO/DMD/Cs₂CO₃/P3HT:PCBM/MoO₃/Al were encapsulated using polyvinyl butyral (PVB), ethylene vinyl acetate (EVA), and thermoplastic poly-urethane (TPU) with a WVTR value of 60, 40, and 150 g·m⁻²·day⁻¹, respectively, and with an OTR value in the range of 10^{-2} – 10^2 cm³·m⁻²·day⁻¹. In this current work, the WVTR and OTR values were not calculated due to different experimental details.

The most common type of an encapsulation method refers to thin film layers encapsulated on top of OPV and perovskite devices using atomic layer deposition (ALD) [19,20]. ALD is particularly suitable for organic and flexible electronics. However, the ALD technique is expensive. Other methods are roll lamination systems encapsulating the OPV devices between two sheets uniting them with an adhesive [21], the other method is based on heat sealing, a process that basically consists of supplying thermal energy on outside of package to soften/melt the sealants [14] and using a glass substrate that is to be sealed with thermosetting epoxy, it could not be effectively applied to flexible devices [22].

Many works have been done for the advancement of good quality encapsulation technologies to stop the migration of environmental oxygen and moisture into device layers. The device lifetime and stability can be improved with high barrier performance encapsulation materials and structures for providing sufficient durability for commercial application. The encapsulation materials with high optical transmission and high dielectric constant need to possess good processing ability. Mechanical strength, good adhesion, and chemical inertness are also required for a suitable encapsulation material.

It is also expected to have low water-absorptivity and permeability and relatively high resistance to UV degradation and thermal oxidation [23]. Organic materials with a good combination of these properties are most commonly used as the encapsulate for the improvement of acceptable device durability [24]. When compared to their inorganic counterparts, the organic encapsulation materials have demonstrated notable advantages, such as the flexible synthesis of the organic molecules by varying their energy levels, molecular weight, and solubility [25]. Organic encapsulation materials are also expendable and they have lesser impact on the environment [26]. Hence, organic materials are the best suitable candidate for the encapsulation of flexible organic and perovskite devices.

2. Degradation Mechanism of OPV and Perovskite Solar Cells

The degradation of organic and perovskite devices can be divided into two mechanisms: intrinsic and extrinsic. Both of these mechanisms are related to mass-transport processes. The metal electrode/active layer interfaces play major roles in the degradation of both devices [27]. Under normal environmental conditions, the relatively high sensitivity of organic and perovskite materials towards oxygen and moisture decrease the device reliability and lifetime.

2.1. Degradation of OPV Devices

Intrinsic degradation: It is due to changes in the structures of the interfaces between layers of the stacking materials, owing to internal modification of the materials used. The key issue is stability, which is limiting the practical applications of OPV devices. The lifetime of OPV devices is now over many thousands of hours. These improvements of lifetime have been achieved with the application of device architecture optimizations and different interface materials, especially after the investigation of hole conductor layers incorporating carbon electrodes. This is promised stable, low cost, and easy device fabrication methods.

Extrinsic Stability: It is affected by the infiltration of air, e.g., oxygen and water. Such degradation from external factors can escalate by light irradiation. There are some organic materials and metal electrodes can also be degraded by oxygen and water. Oxygen or moisture can be trapped during the fabrication processes or they could diffuse into the cell structure during device lifetime. Due to the following factors, oxygen strongly influences the extrinsic stability in some OPV devices [28]: (i) fullerene molecules are hydrophobic and does not react with water; (ii) the exposure to oxygen in air has negative impact on the electron-transport properties of fullerene; and (iii) oxygen forms surface dipoles and increases the metal work-functions. The abovementioned properties yield in the deterioration of the performance of conventional OPVs; however, they might initially enhance the performance of inverted OPV [11]. The chemical degradation processes are the degradation of the metallic electrodes, degradation of the transparent electrode, intermediate hole extraction layers, and/or even the chosen method to synthesize the materials [29,30]. Although it is well-known that oxygen is typically a p-type dopant in semiconductors, the oxygen vacancies act as electron donors [31]. The electronic properties of semiconducting p-type layers might be improved briefly upon exposure to oxygen [32]. To overcome this issue, researchers have developed inverted OPV devices [33,34]. In a humid environment, the oxide layer can double in thickness, and hence block charge-tunnelling. Unlike the abovementioned positive/negative effects of oxygen, there is hardly any positive impact of water on OPV devices that has ever been suggested. Encapsulation delays the process of degradation, but the currently available materials used for encapsulation. The overall device degradation is not stopped, even by a complex encapsulation schemes, such as a sealed glass container or a high vacuum chamber are employed, because the processes involving water and oxygen are efficiently alleviated. The physical and chemical characteristics of the constituent materials are a complex phenomenon. Several processes may take place simultaneously in both physical and chemical characteristics [35].

2.2. Degradation of Perovskite Devices

There are several issues that are related to the degradation of PSCs, such as interface and device instability. These must be addressed to achieve good reproducibility with high conversion efficiencies and long lifetimes of PSCs. A comprehensive understanding of these issues in PSCs is required to achieve stability breakthroughs for practical commercial applications. For the PCE improvement, the stability of PSCs has to be improved for successful small- and large-scale applications.

The degradation of PSCs can occur as a result of intrinsic and extrinsic stability, such as thermal instability (intrinsic stability) and susceptibility of the perovskite material to ambient conditions (e.g., oxygen and humidity). Degradation can occur by other device structure components, such as the degradation of the ETL (TiO_2 or ZnO) at the interface upon light irradiation and the lack of stability of the hole-transport material [36,37]. The stability of perovskite thin films and PSCs has been widely studied [38–40], which includes the degradation of the perovskite material upon exposure to illumination, humidity, or increased temperature [41–44]. Different schemes have been investigated to enhance the stability of PSCs, such as replacing the mesoporous layer [45], modifying the composition or deposition process of perovskite material [46–49], using various charge-transport materials [50–55] and carbon-based electrodes [46], and interfacial layers and/or surface treatments [56–59]. In most of the researches on stability, the stability tests were reported after the devices being stored in the ambient or dark with measurements of the device performance at regular intervals [52,54,55,60]. The report on encouraging stability of the perovskite devices, such as 0.3% PCE drop in one month, often involves storing them under dark in a low-humidity desiccator [39].

However, it is now well established that PSCs are very susceptible to high humidity. The degradation is notably quicker under high humidity conditions [61,62], and it is much faster under continuous illumination than degradation involving storage in the dark [56,62]. Even the degradation under ambient illumination is significantly faster when compared to dark storage [63]. Since there is no standard testing protocol for reporting stability test results, it is strenuous to draw comparisons directly between test results from different publications. For example, Zhu et al. performed stability tests under constant illumination over a short time period in an N_2 glovebox to prevent the intrusion of humidity [62]. Thermal stability has been reported without exposure to illumination or humidity, or a combination of thermal stress and illumination [64]. In some studies, a white light-emitting diode (LED) was used for the illumination, not a solar simulator [50]. The stability can be over-estimated under illumination, owing to the absence of strong UV component in the emission spectrum. The degradation of the perovskite film is reportedly slower under illumination when a UV filter is used in order to eliminate the UV component from the simulated sunlight illumination [43]. Some works have applied several stress factors at the same time during the tests. The factors include constant illumination, ambient humidity of +50%, and increased temperature [65]. Moreover, the moderately humid environment has been used to obtain outdoor testing results [66].

Multiple stability tests have been performed on cells under low ambient humidity without encapsulation, typically under dark conditions [38,46–49], with very few exceptions [50,57,67]. After several hours, devices without encapsulation generally displayed severe degradation under continuous illumination whilst encapsulated devices showed a relatively longer lifetime [39]. In comparison to fully encapsulated devices with a protected edge, partially encapsulated devices showed a shorter lifespan [46]. This signifies the importance of complete encapsulation in order to enhance extend the lifetime of OPV and perovskite devices. However, the comprehensive comparison between different encapsulation techniques for PSCs is still rare [65]. A careful and complicated encapsulation system, developed by employing the combination of a desiccant material and UV epoxy resin, exhibited significantly improved stability. However, the device performance quickly decreased to <50% of the initial efficiency within 10 h under constant illumination and at an ambient humidity of 80% and cell temperature of 85 °C [65]. The absence of standardized testing conditions and studies regarding the effect of encapsulation on the device stability is hampering the advancements of stable organic and perovskite cells. Various encapsulation methods have been investigated for common perovskite

devices that include planar TiO_2 on fluorine doped tin oxide (FTO) glass, methylammonium lead iodide (MAPbI_3) as the active layer, and tetrakis[*N,N*-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-OMeTAD) as the hole transport layer (HTL) [43]. The international summit on OPV stability (ISOS) was followed for the organic solar cell testing (ISOS-L-2 and ISOS-O-1) [68].

2.2.1. Thermal and Photo Stability

It is found that the photo-stability of perovskite materials is a serious problem for the application of PSCs. The perovskite material begins to decompose into PbI_2 at temperature 140°C [69], and even at temperature 85°C when it is heated in nitrogen for 24 h [41]. The slight heating of perovskite materials improved the performance of devices due to the formation of a small amount of PbI_2 which passivate the perovskite. The device performance may be recovered if it is stored in the dark for a short time. Poor photo-stability of perovskite materials could be raised from the local phase change under an elevated temperature when exposed to light. The dual ion hybridization by compositional material engineering at two sites (A and X) simultaneously can solve the perovskite materials stability. The existing ionic components within the perovskite crystal structure would be partially substituted by analogous ions of similar electronic properties, which would passivate the vulnerable sites present within the structure and thereby eliminating the degradation pathways efficiently from the inside-out. For example—the existing monovalent (A-site) organic cation would be partially substituted by metal (Caesium, Cs^+) ions. It has been experimentally proved that heat rather than moisture was the main cause of PSC degradation [70]. The key stability of PSC is to prevent the escape of volatile decomposition products from the perovskite solar cell materials. Polyisobutylene (PIB) encapsulation is one of the promising low cost and low application temperature packaging solutions for PSCs.

2.2.2. Ion Movement

Ion migration in the perovskite materials is another critical issue for the PSCs [71]. The ions (anion or cation) in the halide perovskite materials can move under bias voltage or thermal drift, causing device instability. A schematic diagram of different ion/defects movements in perovskite device structure is shown in Figure 3.

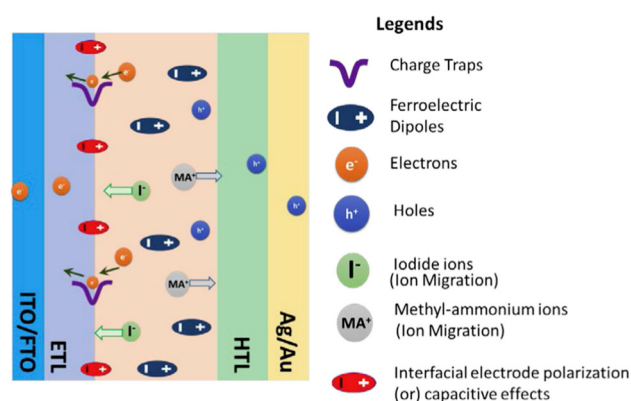


Figure 3. Schematic diagram shows the various ion/defects movements in perovskite device structure that could possibly lead to hysteresis phenomenon during current-voltage characteristic measurements. The exact nature of each ion-movement processes and its degree of influence on hysteresis varies with respect to the device structure and materials involved. Reprinted with permission from [71]. 2018 Solar Energy Materials and Solar Cells.

This defects/ion migration, such as iodine vacancies across the interface, can induce interfacial degradation. This defect migration affects device operational mechanisms and finally cause device failure during operation [9,72].

2.2.3. Electrode Degradation

The interfacial stability of PSCs is also critical for the overall device stability. Recently, it has been found that reactions between iodine-based decomposition products, such as HI from perovskite materials, and traditional metal electrode materials, such as Al or Ag, can lead to the formation of AlI_3 or AgI , respectively [55]. The formation of AlI_3 or AgI compound escalates perovskite decomposition when the material is exposed in an ambient environment (Figure 3) [55]. One way of enhancing the device stability is to insulate the perovskite material from the electrode (Ag/Al). The dispersal of halide ions in PSCs through the charge transport layers could exert a negative impact on the long-term stability of cells.

2.2.4. Charge Transport Layers Degradation

The reasons behind poor device stability of PSCs are due to either the perovskite materials or charge transport layer interfaces. Organic semiconductor layers in the PSC structure that are used as charge transport layers (ETL and HTL) are prone to both oxidization and water absorption that can reduce the device stability. For example, an n-type fullerene, PCBM was used as an efficient ETL in an inverted structure PSC [73]. The authors found that the PCBM went through changes in terms of chemical states or band structure in ambient air, which was a major contributing factor to the device degradation [73]. A p-type organic semiconductor, PEDOT:PSS, is generally used in the inverted structure as the HTL. PEDOT:PSS has high water absorptivity and acidic properties causing etching of the transparent conductive electrode, such as ITO. The hygroscopic and acidic nature of PEDOT:PSS accelerates device degradation [55,74]. Lithium (Li) doped Spiro-OMeTAD salt is also hygroscopic and can diffuse water into the light absorbing perovskite layer causing device failure [75]. Several investigations suggested that oxygen de-absorption from TiO_2 surface (degradation of TiO_2 layer), while light soaking leads to failure of devices [45]. Multiple techniques have been employed for the improvement of the device stability [7,74]. Idigoras et al. [76] deposited thin polymer layer by the remote plasma vacuum deposition of adamantane powder for the encapsulation of perovskite solar cells. They observed that the deterioration of device performance was significantly delayed because of the encapsulation layer.

Bella et al. [77] investigated the stability of PSCs by encapsulation of photochemical resistance as well as moisture tolerance, a fluoro-polymeric light-curable coating on the back contact side. The use of the fluoro-polymeric layer on top of the PSC has the prospect of preventing the oxygen and moisture migration between the top back contact and the perovskite layer due to the hydrophobicity of the coating. The fluoro-polymeric UV-coating possesses a cross-linked nature that can lower the free volume when compared to the traditional non-cross-linked, polymeric systems. Hence, it is expected to improve the long-term stability of PSCs [78]. Figure 4 displays the test results of device stability in terms of PCEs under various atmospheric conditions and photochemical external stresses during 180-days (4320 h). Moreover, those encapsulated devices were tested in outdoor conditions for a time of >3 months (i.e., 2160 h). Successful tolerance toward heavy rain, soil, and dust were observed on the external surface made of glass. In real outdoor conditions, the fluorinated luminescent down shifting layer with low-surface energy helps to clean the front electrode easily.

Uncoated and front-coated devices were studied for an overall period of six months in the aging test. The devices were stored in a glove box filled with Ar for the first three months. The devices were continuously illuminated for 8 h every day with a UV optical fibre with light intensity $5 \text{ mW} \cdot \text{cm}^{-2}$. 5% contribution from the UV light source (280–400 nm) helped to simulate the solar spectral irradiance on Earth (AM1.5G , $1000 \text{ W} \cdot \text{m}^{-2}$). In the forced UV aging test (Figure 4), the uncoated devices (black curve) had a reduction of 30% in their initial efficiency after one week of UV exposure and stopped working after one month. All of the five front-coated cells (red curve) retained 98% of their initial PCE, even after three months and demonstrated excellent stability under the same conditions.

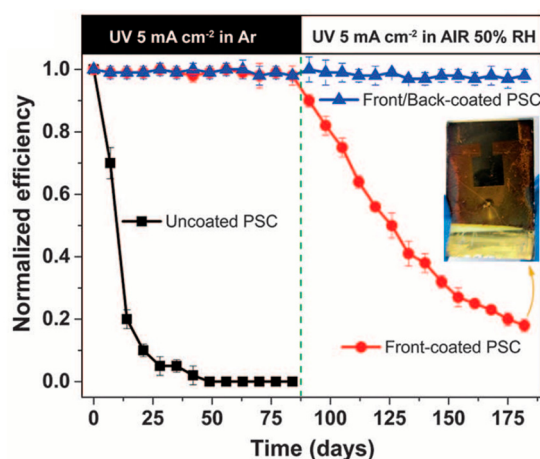


Figure 4. The aging test results on the three series of PSCs: (i) uncoated, (ii) front-coated with a luminescent fluorinated coating, and (iii) front/back-coated (front coating with the luminescent fluorophore and back contact coating with a moisture resistant fluoro-polymeric layer). The cells were stored in an Ar environment during the first three months of the test period. They were kept in the air with RH = 50% for the next three months. During the whole testing period, the PSCs were exposed to continuous UV illumination. The device power conversion efficiency (PCE) was recorded once a week. The inset shows a photograph of a front-coated solar cell at the end of the test. Reprinted with permission from [77]. Copyright 2018 American Association for the Advancement of Science.

By simple visual inspection, the effects of degradation were easily detectable. The progressive yellowing was observed in the mixed-perovskite layer upon 50% RH exposure. The back-contact side was coated with a fluoropolymeric light-curable coating in the front/back-coated devices for stabilizing the devices with enhanced photochemical resistance and moisture tolerance. A similar method was used in the luminescent downshifting experiment for back-coated PSCs. It is hypothesized that the use of highly hydrophobic fluoropolymeric layer on the PSC top can prevent water permeation from the top back contact to the perovskite layer. In addition, the fluoro-polymeric UV-coating possesses a cross-linked nature, leading to lower free volume when compared to the traditional non-cross-linked, polymeric systems. Hence, the coating is expected to improve the long-term stability of PSCs [79]. The aging test results of the front/back-coated PSCs (blue curve), i.e., devices with a luminescent coating on front and a moisture-resistant coating on the back contact, is shown in Figure 4. Even under the combined effects of photochemical and environmental stresses, all the five devices retained exceptional stability of 98%.

The front/back-coated PSCs showed longer lifetime stability retaining most of their initial efficiency the ageing test due to the following reasons:

- securing the perovskite material from UV irradiation and converting it into visible photons;
- shielding devices from oxygen and moisture, hence blocking the hydrolytic behaviour of the perovskite material;
- maintaining clean front electrode clean by the self-cleaning characteristics of this fluorinated polymer. Similar results were also observed for outdoor tests performed.

The non-homogeneous deposition of the coating layers on the front/back side of the device can cause slow hydrolysis of the active perovskite layer. To test the homogeneity of the deposited coating layer, Bella et al. [77] dipped the devices with front/back coatings into the water for about a day. No change in photovoltaic performance was observed in the front/back-coated devices, even after one day of immersion in water.

3. Encapsulation Requirements

To ensure satisfactory encapsulation (Table 1), the permeation of WVTR and OTR needs to be two-three orders of magnitude lower than the bare substrate. Silicon-based dielectric films, deposited by PECVD, have reportedly demonstrated excellent transparent, single-layer barrier performance [80]. However, on polymer substrates it is very difficult to obtain permeation levels that are 1000 times lower by a single layer barrier. The increase in single-layer barrier thickness results in an OTR value that is on-zero asymptotic and is governed by the defects in the barrier layer. Such defects are typically generated from the intrinsic or extrinsic roughness of surface [81]. Hence, the performance of single-layer, encapsulated gas barriers is controlled by the nano-meter size structural defects. In theoretical calculations, the total permeation rate is much higher due to a large number of small pin-holes than that from few but larger defects in the same total pin-hole area [82]. The lateral diffusion of gas is more crucial when the defect diameters are smaller than the substrate thickness. The multilayered deposition of inorganic materials can slightly enhance the performance of the encapsulation barrier. The deposition of organic–inorganic multilayers films to obtain increased barrier performance is the most common practice [83]. However, there are several challenges in the way of utilization and development of thin-film encapsulation. To face these challenges, a variety of materials have been developed to improve the device lifetimes, such as titanium oxide (TiO_x). Using thin films as barriers for device encapsulation is not sufficient for the protection of organic and perovskite devices. The use of glass plates as encapsulation is the simplest and best example for the protection of oxygen and moisture. Glass encapsulation can supply the required oxygen and moisture protection in the organic and perovskite solar cells for commercial application. However, glass encapsulation cannot apply on inflexible devices. It has also been shown that a thin layer of SiO_xC_y acts as a barrier for oxygen and moisture. Unfortunately, the PECVD process is required for the deposition of this encapsulation film, which is expensive and uses complicated vacuum systems. This is also not suitable to deposit on a flexible substrate as a barrier of oxygen and moisture transmission. Although there are other encapsulating materials, they cannot fulfil the barrier requirements for organic and perovskite solar cells. In this review paper, we have presented different encapsulation materials used in various approaches and integrated with organic and perovskite devices. In Table 2, we have summarized some of the polymer materials with their WVTR values for the organic and perovskite solar cells. Recently, using the RF plasma polymerization technique linalyl acetate [84,85] and terpinene-4-ol thin films has been deposited for the encapsulation of devices. On the basis of surface and optical properties, these polymer based thin films can be potential encapsulating layers for organic and perovskite solar cells [86,87].

Materials for Encapsulation

The encapsulation materials should have high a dielectric breakdown that matches the refractive index with other layers and high volume resistivity. Materials should be low cost, dimensionally stability, and easy to deposit. WVTR and OTR represent the steady state rates at which water vapour and oxygen gas, respectively, penetrate through the encapsulating film that affects the encapsulation layer. Glass transition temperature (T_g) for organic encapsulation material is another important property, which is dependent on the chain flexibility. The polymer mechanically varies from being rigid and brittle and becomes tough and leathery. The maximum exposure temperatures on encapsulation material and the effect on the mechanical behaviour of the material should be known. The light transmission through the encapsulation materials is also important to measure to understand how it will affect the device performance. The encapsulation material requirements are also to define the UV absorption degradation, hydrolysis, and some other aspects. A list of suitable polymer encapsulation materials and their specifications for the roll-to-roll fabrication of devices are given below.

Table 2. List of probable polymer encapsulation materials for organic photovoltaic (OPV) and Perovskite devices.

Materials	Encapsulation Type	Water Vapour Transmission Rate (WVTR) ($\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)	Comments	References
Ethylene vinyl acetate (EVA)	Single layer encapsulation	40	Light transmission of 91%. Suitable for resisting weather and long-term reliability under light exposure. It is suitable for encapsulation of organic and perovskite solar modules.	[88,89]
Europium doped EVA: Eu^{3+}	Single layer encapsulation	40	Absorption bang gap is 310 nm (4 eV). Suitable for PV module encapsulation. Eu^{3+} doped EVA layers can induce photon down-shifting with wavelengths <460 nm.	[90]
Ethylene methyl acrylate (EMA)	Single layer encapsulation	Not mentioned	EMA is suitable for chemical resistance, thermally stability, adherence to different substrates and excellent mechanical behaviour at low temperature. It is suitable for encapsulation of perovskite and organic devices.	[23,91]
Polyvinyl butyral (PVB)	Single layer encapsulation	60	PVB has high optical transparency, good heat resistance, good adherence to solar cells, glass, and other plastics, increased bond durability, and compatible with module components. PVB is already used as encapsulation layer for thin film solar cells.	[14]
Thermoplastic polyurethane (TPU)	Single layer encapsulation	150	TPU film is better than EVA film for encapsulation since it is flexible to bond with relatively hard materials. These films can be processed in normal atmospheric pressure without cross-linking and emissions.	[92,93]
UV-cured epoxy	Single layer encapsulation	16	Epoxy film is good for encapsulation. It is optically transparent, thermally conductive, weather resistance, high temperature resistance, good adhesive properties on glass and plastic.	[70]
Polyisobutylene (PIB)	Single layer encapsulation	0.001–0.0001	PIB is a synthetic rubber. It can encapsulate organic and perovskite solar cells.	[70]
Cyclized perfluoro-polymer (Cytot TM)	Single layer encapsulation	Not mentioned	Conventional thin-film deposition techniques e.g., spin coating can be used to deposit this polymer. It is transparent and amorphous. This material is good for weather resistant, good for oxygen/ water-vapor shielding for testing organic device lifetime.	[94]
Organic–inorganic hybrid materials ORMOCERs (ORM)	Single layer encapsulation	0.01	It is organic and inorganic components modified ceramics or ORM. It has good chemical resistance, highly transparent, anti-soiling, diffusion- inhibition. OTR is $<0.01 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$. These properties are necessary for the encapsulation of organic and perovskite solar cells.	[95,96]
ORMOSIL aero-gel thin film	Single layer encapsulation	Not mentioned	It is mechanically and thermally stable and highly transparent. ORMOSIL materials are flexibility and stability at atmospheric conditions. ORMOSIL has variable organic group that can modify the chemical and physical surface properties.	[97,98]
Other organic materials	Single layer encapsulation	Not mentioned	Encapsulation tested of 10 polymers were poly(vinyl methyl ketone) (PVMK), poly(methyl methacrylate) (PMMA), poly(vinylidene chloride-co-vinyl chloride) (PVDC-co-PVC), poly (vinylidene fluoride)(PVDF), polyacrylonitrile (PAN), poly(vinylalcohol) (PVA), poly(vinylphenol) (PVP), poly(methyl vinyl ether) (PMVE), polystyrene (PS), and poly(vinyl chloride) (PVC). An encapsulation approach with these 10 low-polarity polymer is demonstrated to block water/moisture and prevent encapsulation-induced degradation.	[99,100]
Luminescent downshifting fluoro-polymeric coating such as PTFE (polytetrafluoroethylene), PFA (perfluoroalkoxy), FEP (fluorinated ethylene-propylene), etc.	Single layer encapsulation	Not mentioned	It is very good as an encapsulating material for organic and perovskite solar cells to improve the device stability for the out-door application. Fluoropolymers are excellent for chemical and thermal resistance. Their surfaces are non-reactive with all chemicals and solvents.	[101]

4. Discussion

Thin-film encapsulation is a vital technology that is required for the application and commercialization of perovskite and organic solar cells. An effective encapsulation is crucial to prevent the permeation of moisture and oxygen to achieve the desired reliability and device lifetime. More progress is needed to develop encapsulating materials for devices with specific requirements. The processing conditions of EVA exposure time and damp heat affect its adhesion strength. Transport of moisture and oxygen through local pinholes become an issue for achieving ultrahigh barriers encapsulation that is hard to be avoided. New encapsulation materials need to be developed to fulfil the encapsulation requirements and achieve ultrahigh encapsulation barriers. Furthermore, the encapsulation processing temperature of thin film should be within the temperature range that is suitable for the organic polymer substrate materials. Usually, low-temperature PECVD processed inorganic encapsulation thin films are not suitable for the encapsulation barrier, since these films suffer from intrinsic defects. Water vapour and oxygen can easily diffuse through these defects. For high performance encapsulation barriers, these intrinsic defects should be reduced or passivated. Inorganic and organic alternating multilayer films can be one solution to reduce and avoid intrinsic pinholes. The defects in the inorganic layers can be passivated by an organic film and do not channel continuously through the multilayer structure. A steady state permeation rate of moisture and oxygen can be maintained by the multilayer encapsulation barrier structures. A transient rate of encapsulation barrier can be maintained over a specific time-period that might exceed the desired lifetime of encapsulated devices. Typically, the permeation rate in the transient region is lower than the permeation rate in the steady state. It is suggested that the barrier performance characterization from the initial transient period will provide an underestimation of the total permeation rate for long-term applications. As a result, the barrier performance in multilayer structures should be characterized separately, such as the steady-state and transient permeation rates. This should be used for the calculation of lag time to avoid overestimation of expected device lifetimes or barrier performance during both storage and application. Moreover, the deposition of high quality inorganic encapsulation layer with vacuum deposition processes is expensive and low through put.

Since there are alternative deposition processes using different deposition chambers for organic and inorganic layers, multilayer barrier structures are expensive. If inorganic layers can be deposited from the solution precursors, it can be a promising solution to this problem, making it possible to deposit inorganic and organic multilayer barriers employing similar deposition techniques. Hence, totally solution process should be developed for low cost, high barrier materials for perovskite and OPV encapsulation. Optimization of the individual film dimension can be useful multilayer encapsulation structures. Before adapting these technologies, the quality of films should also be improved. The reliability and continuous yield of encapsulation processes must be explored to reduce the processing steps and time. Since perovskite and organic solar cells are very susceptible to moisture, it is crucial to use a low-diffusivity edge seal material.

Graphene is a carbon-based one-dimensional material with excellent electronic and mechanical properties offering limitless opportunities in device engineering. In line with this, graphene can be used as a bi-functional electrode that will serve as a highly conductive charge collection electrode as well as an encapsulant for the underlying organic or perovskite layers. This carbon-graphene based encapsulation technology is sought to be a viable approach for large scale commercialization and deployment of organic and perovskite solar cells technology.

5. Conclusions

Effective thin film encapsulation is crucial to prevent the permeation of water vapour and oxygen for achieving the stability and desired life times of organic and perovskite solar cells. The problem of achieving a thin layer encapsulation barrier is transport-dependent permeation through localized pin-holes that is strenuous to control. New materials and technology are required to satisfy the requirements of encapsulation to prevent the permeation of moisture and oxygen for the reliability

and stability of devices. The encapsulation processing temperature of thin film should be within the temperature range suitable for the organic and polymer substrate materials. Multilayer polymer films of encapsulation can be a solution to block the pinholes in the films to stop the permeation of water vapour and oxygen. However, the barrier performance of multilayer structures encapsulation consists of a steady state permeation rate as well as a transient rate over a specified time. These rates of encapsulation barrier can exceed the desired lifetime of encapsulated devices. The barrier performance in multilayer structures should be characterized separately by the steady-state and transient permeation rates over a specified time-period. Multilayer thin film encapsulation structures deposited under vacuum will be exorbitant, owing to alternative deposition of layers in separate deposition chambers. Solution process deposition can be a promising alternative for low-cost barrier materials for thin film multilayers encapsulation. Subsequently, multilayers can be deposited with a similar deposition process to obtain low-cost barrier materials. Film quality should be improved before adopting the multilayer encapsulation technologies. Encapsulation layers with high quality are significant to improve the device lifetimes.

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