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Perspective

Encapsulation and Stability Testing of Perovskite Solar Cells for Real Life Applications

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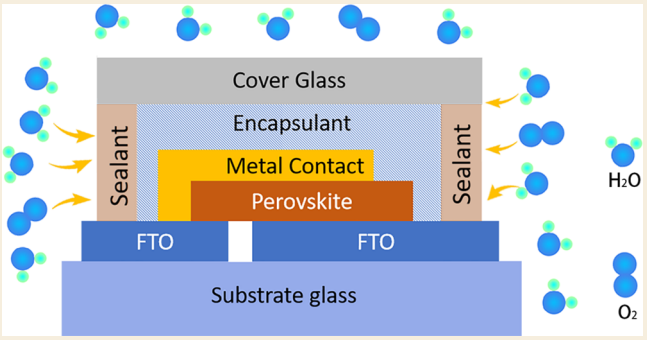
ABSTRACT: With the progress in the development of perovskite solar cells, increased efforts have been devoted to enhancing their stability. With more devices being able to survive harsher stability testing conditions, such as damp heat or outdoor testing, there is increased interest in encapsulation techniques suitable for this type of tests, since both device architecture compatible with increased stability and effective encapsulation are necessary for those testing conditions. A variety of encapsulation techniques and materials have been reported to date for devices with different architectures and tested under different conditions. In this Perspective, we will discuss important factors affecting the encapsulation effectiveness and focus on the devices, which have been subjected to outdoor testing or damp heat testing. In addition to encapsulation requirements for these testing conditions, we will also discuss device requirements. Finally, we discuss possible methods for accelerating the testing of encapsulation and device stability and discuss the future outlook and important issues, which need to be addressed for further advancement of the stability of perovskite solar cells.



KEYWORDS: *perovskite, stability, encapsulation*

1. INTRODUCTION

Perovskite solar cells (PSCs) have rapidly advanced to achieve high efficiency exceeding 25%.[1] Despite high efficiency, significant challenges exist for the future commercialization of perovskite solar cells, namely, long-term stability, lead toxicity, scalability, and reproducibility.[1] Stability in particular has attracted significant attention, since the perovskite films and devices are known to exhibit poor stability when exposed to elevated temperature, illumination, and ambient atmosphere (moisture, oxygen).[1]

However, while there are numerous reviews on perovskite stability (76 from 2019 to date), reviews on encapsulation[2−8] have been scarce (5 from 2019 to date), where the numbers are obtained via a *Web of Science* search using keywords "perovskite and stability" or "perovskite and encapsulation" in the title of the article (corresponding numbers with keywords in the topic are 830 for stability, 55 for encapsulation, but these also include many papers not dealing with solar cells). Thus, despite the fact that encapsulated cells exhibiting long-term outdoor stability are needed for practical applications, reports on both encapsulation and outdoor testing have been scarce. Nevertheless, some form of stability testing is commonly performed when reporting on PSC research. However, the majority of the works simply perform testing involving storage in the ambient, commonly in the dark between the measurements, and stability characterizations inside the glovebox are common. For example, a literature search in *Web of Science* with keywords "Perovskite and (solar or photovoltaic)" reveals 194 papers published in February 2021, out of which 112 reported experimental work on solar cells, 49 do not provide long-term stability characterization (for various reasons, including different focus of the work), and 53 provide ambient stability (in 51 case for devices without encapsulation), and 5 provide stability in inert atmosphere (this is commonly performed at elevated temperature). For testing under illumination, tests in an inert environment have been reported in 11 papers, tests in ambient for encapsulated devices were reported in 3 papers, and tests in ambient either without describing clearly if there is encapsulation or with only performing the test for a short time were reported in 8 papers. In the same time period, there have been three reports of damp

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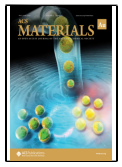

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heat tests (one also including illumination under Xe lamp solar simulator (100 mW/cm^2 AM 1.5G[9]), while there have been no reports on outdoor testing. Compared to the early days of perovskite research, stability testing practices have improved, but obviously there is a need for further improvements, particularly in terms of standardization of the testing conditions and more common use of harsh testing conditions instead of simple shelf life tests.

It should also be noted that tests in an inert environment remain relatively common, although less common than dark ambient storage. The rationale for this practice is that the measurements performed inside the glovebox reflect the true intrinsic stability of the device, while for encapsulated devices measured in ambient it would be difficult to establish if the reduction in the efficiency or failure occurred due to extrinsic factors (encapsulation failure) or intrinsic device instability. While developing the understanding of the intrinsic device stability is important (and hence testing in inert atmosphere is suggested for addressing the intrinsic stability in ISOS protocols[10,11]), it is also important to develop effective encapsulation to achieve the demonstration of stable performance of encapsulated devices in ambient (preferably outdoors) and to pass standard performance tests such as the damp heat test. It should also be noted that the presence or absence of encapsulation can affect the lifetime of the devices even in an inert environment since encapsulation can prevent the escape of volatile degradation products,[11−13] and it is also necessary to consider how the inert environment testing is achieved. The basic premise that a glovebox environment is an inert clean atmosphere and hence measured stability represents intrinsic device stability is not necessarily true, unless characterization is performed inside a glovebox system separate from the fabrication system and with independent circulation to avoid any effects of residual solvent. If the device characterization and spin-coating or solution preparation are performed in the same or connected gloveboxes, the atmosphere inside is affected by the usage (frequency, amount and types of solvents used) and maintenance practices (frequency of regeneration and active carbon replacement). This compounds the difficulties in reproducing the reported results arising from glovebox atmosphere and tiny deposition details effect on the perovskite films properties. Due to the lack of attention devoted to encapsulation and the lack of standardized encapsulation approaches, the characterization of the stability of encapsulated devices would also result in variations in stability reports due to variations in encapsulation techniques, but at least the reported results would have greater practical relevance.

Furthermore, an overwhelming majority of the reported work in the literature on encapsulation of PSCs is concerned with the lab-scale encapsulation of relatively small devices and many techniques used are different from the methods and materials used in commercial devices for other technologies. Therefore, we will also discuss encapsulation methods actually used in commercial devices for other relevant technologies. What we aim to achieve in this Perspective is to provide a detailed discussion of encapsulation methods relevant for stability tests under harsh testing conditions (damp heat and outdoor testing) and provide descriptions of the experimental practices and common problems. Since the achievement of high performance solar cells has become more common after recent detailed sharing of the experimental procedures for devices with power conversion efficiency over 20%,[14] we would like to encourage wider adoption of encapsulation by not only discussing results reported in the literature but also by sharing detailed experimental practices and common problems. Then, we briefly discuss the recommendations for the stability testing, followed by an overview of stability reports for harsh testing conditions (damp heat and outdoor testing). Finally, we discuss outstanding issues and future outlook.

2. LESSONS LEARNED FROM OTHER TECHNOLOGIES

We will briefly summarize encapsulation solutions which have been applied to existing commercialized technologies, such as organic light emitting diodes (OLEDs) and various photovoltaic (PV) technologies. We will also briefly mention organic photovoltaics (OPVs), which have not yet been commercialized.

2.1. OLEDs and OPVs

OLEDs are known to be extremely sensitive to moisture, requiring a water vapor transmission rate (WVTR) of the order 10^{-6} g/m^2/day, which is lower than the sensitivity limit of common commercial WVTR measurement instruments (order of 10^{-4} g/m^2/day) and significantly lower than the WVTR needed for liquid crystal displays and photovoltaics.[15] As a consequence, OLEDs require high quality sealing with a low WVTR material, and the packaging commonly contains a cavity with a desiccant.[15] The inner cavity can be filled with inert gas (edge seal) or filled with resin, where a passivation layer is typically needed.[15] The cavity structure with an edge seal is typically used for applications in watches, phones, and tablets, while a no-cavity resin-filled structure is of interest for large and/or flexible displays.[15] The cavity structure as mentioned requires a desiccant sheet, and metal or a glass cap is usually used as a cover, while epoxy resins or a glass frit are used as edge sealants.[15] Multiple cavity structures (Russian doll architecture) can also be used,[16] but this would inevitably increase the cost. In resin-filled encapsulation, due to the absence of desiccant and insufficient barrier properties of resin, typically an additional passivation layer deposited on top of the devices is needed for moisture protection.[15] In addition, film-based encapsulation, consisting of alternating layers of organic and inorganic layers, is of interest for flexible display applications.[15]

OPV devices share similar approaches to encapsulation as OLEDs, with the difference being that cover glass rather than a metal cap is typically used.[16] Also similar to OLEDs, there is a lot of interest in the development of film-based encapsulation, which includes various thin film barrier solutions developed for OLEDs, such as Cytop, ORMOCER, ORMOSIL, etc.[16] Additionally, the use of various epoxies, including in particular the UV curable epoxies, is common.[17] In addition to sharing some of the encapsulation strategies with OLEDs, similar approaches to other PV technologies have been adopted, using common encapsulants such as ethylene vinyl acetate (EVA) and polyvinyl butyral (PVB).[16] For a summary of encapsulation of OPV devices, see refs 8, 16, and 17.

An important thing to note is that while halide perovskites share the sensitivity to moisture common for OLEDs, the required lifetime for displays (several years) is much shorter compared to that of PV modules (20−25 years). Nevertheless, application of similar materials and packaging designs used in OLEDs and OPVs to PSCs is relatively common, in particular the use of various epoxies.

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Table 1. Reported Properties of Different Encapsulation Materials[a]

encapsulation material	WVTR (g/m^2 day)or K (cm/h$^{1/2}$)	T_g (°C)	T (%)	elastic modulus (MPa)	harmful byproduct	ref
EVA	WVTR = 2.61, $WVTR_{85}$ > 10−1000, K = 0.38	−31	93	10	acetic acid	13, 19, 29, 33, 34
Surlyn	$WVTR_{20}$ ∼ 1		93.4	394	methacrylic acid	13, 33
POE 3M	$WVTR_{38}$ ∼ 0.8 (g mm/m^2 day)	−34 to −44	91	9.1	unknown	13, 30, 34
POE CVF			92	20	unknown	13
POE ENLIGHT			>85	7	unknown	13
PDMS	$WVTR_{20}$ > 100, K = 0.8	−160	∼94	1.4−3.3	unknown	20, 34, 35
TPU	K = 0.23	2	∼94	7.3−8.7	unknown	20, 34, 36
Ionomer 1	$WVTR_{85}$ ∼ 1, K = 0.067		∼93		unknown	20, 29
PVB	$WVTR_{85}$ ∼ 10, K = 0.25	15	∼94	1.0−2.9	unknown	20, 29, 34, 37
PIB	K = 0.018−0.024	−73	0	∼0.6	unknown	20, 38, 39

[a]WVTR denotes water vapor transmission rate (with subscript denoting temperature of measurement), T_g denotes glass transition temperature, K denotes moisture penetration depth. T_g values for POE samples are given as a range since the type of POE has not been specified. Values obtained from ref 33 correspond to 100 μm thick films at 20 °C. In addition, the properties shown would depend on various additives, and transmittance would also depend on the thickness of the encapsulant, so some variation from the numbers shown is expected for material obtained from different suppliers. PIB transmittance is given as 0, since PIB for PV encapsulation is normally supplied with carbon filler and is nontransparent.

2.2. Commercial PV

Commercial silicon devices typically use vacuum lamination between two pieces of glass or a single piece of glass and a back plate, using an encapsulant and edge sealant.[8] The lifespan of glass-laminated panels is significantly longer compared to polymer laminated ones (typical polymers are polyethylene terephthalate (PET) and ethylene tetrafluoroethylene (ETFE)),[18] which is why we will mainly discuss encapsulation involving a glass cover. Similar materials and processes are used for Si PV as well as other PV technologies, such as CIGS.[19,20] The purpose of the encapsulant is to provide mechanical support and/or good adhesion to the cover,[21] provide electrical isolation, protect cells from moisture, and ensure good mechanical seal over a range of temperatures and humidities,[22] while the purpose of edge seal is to prevent moisture ingress.[21] Some materials with low WVTR are not suitable as encapsulants due to a high mechanical modulus, since a low mechanical modulus of the encapsulant at all temperatures is needed to accommodate mechanical stress.[20,21]

Conventional PV technologies, in particular crystalline Si cells, possess sufficient lifetime, but further progress is needed in their encapsulation to lower their cost and reduce their degradation rate further. A significant drawback of the conventional encapsulation is the time needed for lamination (in the range 8−20 min)[23,24] as well as high capital cost and large factory footprints for laminators for high volume PV production.[24] For example, a typical factory with a capacity of 3GW/year needs 15 laminators at a capital cost of 180 million USD.[24] Thus, different materials and process modifications have been investigated. In the early development of Si solar cells, polydimethylsiloxane (PDMS) was used as an encapsulant, and later it was replaced by EVA to reduce module and manufacturing cost.[20] EVA has been used as a common encapsulant, but this is not necessarily because EVA has superior properties but rather because it represents a low cost option with acceptable durability.[20] EVA encapsulated modules typically face degradation due to delamination and/or cracking of the glass, as a consequence of the acetic acid byproduct.[25,26] For that reason, it has been suggested that, in particular for glass-glass encapsulation, ionomers or polyolefins are more suitable materials.[26] Acetic acid also contributes to the degradation of the metal contacts and even results in the lead leaching out of the glass and the formation of lead acetate and lead carbonate composites.[27]

More recently, there has been increasing interest in polyolefin elastomer-based (POE) encapsulant as well as other alternatives to EVA such as ionomers, PVB, and thermoplastic polyurethane (TPU).[20] Silicone-based encapsulants are also of interest, since they exhibit higher durability compared to hydrocarbon materials due to a higher dissociation energy of S−O bonds compared to C−C bonds.[20] Among these, TPU has demonstrated better performance compared to EVA under damp heat testing[28] while PVB has been found to be sensitive to hydrolysis,[29] which could cause problems for aging in high humidity environments. POE is of interest as a replacement for EVA, due to the fact that it does not produce acetic acid, can result in faster lamination processes, and results in lower potential induced degradation (PID).[20] PID was reported to depend on the resistivity of the encapsulant, which can range between 10^{13} and 10^{15} for EVA and 10^{13} and 10^{17} for POE.[20]

Properties of common encapsulant materials are listed in Table 1. It should be noted that these properties can be further adjusted by using different additives, such as cross-linkers, plasticizers, adhesion promoters, UV absorbers, and/or radical scavengers.[20] Another point to note is that cross-linked encapsulants can be chemically bonded to the surfaces in addition to the ionic, hydrogen, and/or van der Waals bonding present in thermoplastic encapsulants and, consequently, they achieve stronger adhesion.[20]

It can be observed from the table that the majority of encapsulant materials listed have a relatively high WVTR or water vapor diffusion coefficient. The water vapor diffusion coefficient has been used to describe how quickly the moisture would penetrate into the module, since the moisture ingress profile was found to be dynamic and not at equilibrium.[30] Thus, edge sealant is needed to protect moisture-sensitive materials. The edge seal needs to have low moisture diffusion and contain desiccant to delay moisture ingress,[21] such as desiccant-filled polyisobutylene (PIB).[20] To illustrate the need for an edge seal, if a typical encapsulant such as EVA or PDMS is used, the breakthrough times for moisture passing through a 12.5 mm seal are 2 days and 1.15 h, respectively.[21] These materials also typically exhibit high oxygen transmission rate (OTR), such as OTR_{85} = 3000 cm^2/m^{2}day for EVA, 400 cm^2/m^{2}day for ionomer, and 5000 cm^2/m^{2}day for PVB.[29] In

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contrast, desiccant-filled PIB capable of achieving 1000 h under damp heat measurements with the seal width of ~ 12.5 mm.[20] However, while PIB edge sealant has low moisture diffusion and forms good adhesion to glass, the strength of the adhesion can rapidly decrease at high temperatures, so that secondary sealant functioning as an adhesive is applied on the edge.[31] Secondary sealants include polyurethane, silicone, and polysulfide.[31] For example, an edge seal consisting of combined PIB and silicone has been proposed to achieve both improved moisture protection and improved mechanical strength.[23] Blending of the PIB and PDMS has also been proposed to achieve optimal combination of properties, such as retaining high adhesion and moisture resistance, while high transparency could be achieved (PIB is typically non-transparent due to incorporation of carbon black fillers which serve as UV absorbers and blockers).[32]

3. ENCAPSULATION METHODS AND MATERIALS FOR PSCs

An ideal encapsulation material should have low OTR and WVTR, no effect on light transmission, suitable mechanical properties which facilitate absorbing strain, high resistance to UV and thermal oxidation, high adhesion to perovskite device/module, and similar thermal expansion coefficient as perovskite materials.[3,6] However, it should be noted that the often cited requirement for high transmittance does not necessarily apply for PSCs on glass substrates where only top cover glass is used for encapsulation, since this requirement is commonly listed for Si module encapsulation where the modules are sandwiched between the two pieces of glass or glass and back panel. Consequently, black PIB tape has been used for PSC encapsulation.[12,13,40−43] On the other hand, due to the high sensitivity of the perovskite materials and devices to ambient exposure, low values for OTR and WVTR, as well as suitable mechanical properties, are critical since delamination would lead to a quick failure. The requirements for OTR and WVTR for PSC encapsulation are stated to be 10^{-4}−10^{-6} cm^3/m^2 day atm and 10^{-3}−10^{-6} cm^3/m^2 day.[6] In addition, the encapsulation material should not react with any PSC components and it should ideally also be capable of lead sequestration. Further, encapsulation process and materials should be scalable and have low cost. In this section, we will discuss the pros and cons of different encapsulation methods and materials to facilitate selection of an appropriate encapsulation method.

3.1. Encapsulation Materials

A variety of encapsulation materials and techniques have been reported in the literature, such as EVA,[2,13,44,45] PVB,[2,8] PIB,[2,12,13,40−43,45,46] fluoropolymeric coating,[2,47] TPU,[2,48] ethylene methyl acrylate, cyclized perfluoro-polymer (Cytop), organic−inorganic hybrid materials ORMOCERs, ORMOSIL aero-gel thin film, various polymer films,[2] PDMS, PET, polytetrafluoroethylene (PTFE), polycarbonate (PC),[3] polyimide (Kapton) tape,[49] Surlyn,[40,50] POE ENLIGHT,[42] oxide thin films deposited by various methods,[51−53] graphene/parylene with PIB edge seal,[54] various UV curable epoxies (Threebond, Vitralit epoxy glue by Panacol, Ossila E132 resin, Ossila Encapsulation Epoxy E131, Norland optical adhesive, Nagase Chemtex),[6,55−59] etc.

Attempts have been made to compare different types of encapsulation, as we will discuss in the following. However, reports on direct comparisons of different encapsulation materials applied in the same method have been scarce, although some comparisons exist. For example, Threebond UV curing Resin 3035B and Ossila Encapsulation Epoxy E131 have been compared, and it was found that Ossila sealant resulted in superior performance.[57] The scarcity of direct comparisons and the variations of testing methods reported in the literature makes choosing an appropriate method difficult, especially since attempts to directly adapt techniques used for encapsulation of other moisture-sensitive materials such as OLEDs do not necessarily result in good device performance in terms of efficiency, compared to the devices without encapsulation.[60] In the early days of PSC research, it was not uncommon to observe a deterioration of device efficiency upon encapsulation, with the degree of deterioration dependent on material and process used,[48,51,60] although this problem can be avoided with appropriate material and method selection and appropriate implementation (such as cleaning up the edges of perovskite film, etc.). The reduction in the efficiency of encapsulated cells likely occurs due to negative effects of the outgassing of the solvent or other components used in the sealant either during curing or during thermal stress.[51,61] To select a suitable encapsulation method, it is highly desirable to observe minimal degradation of the efficiency compared to devices without encapsulation and that the reported encapsulation method has been found to be effective under rigorous stability tests, such as damp heat tests or outdoor testing.

3.2. PSC Encapsulation Methods

Successful encapsulation typically does not result in significant changes of efficiency after encapsulation.[62,63] For example, ~19.2% average efficiency was obtained for 16 cells before and after encapsulation, with the best device exhibiting 19.9% PCE efficiency before 19.7% efficiency after encapsulation.[62] In tandem cells, some drop in the efficiency can occur after encapsulation due to front glass reflection,[64] but this mechanism is not applicable to individual PSCs which are typically illuminated through the same glass substrate before and after illumination. If more complex packaging is used with additional interfaces introduced on the illumination side, some efficiency drop due to optical losses in the packaging could occur. Therefore, careful package design to minimize optical losses and the use of antireflective coatings are desirable in tandem devices and devices using packaging with additional interfaces introduced at the illumination side compared to unencapsulated cells.

The encapsulation methods for lab scale encapsulation can be divided into two categories: stand alone (thin) film encapsulation and cover glass encapsulation (or flexible cover encapsulation). Depending on how the cover glass is attached, cover glass encapsulation can involve two main types, namely, blanket and edge encapsulation, and their combination, as illustrated in Figure 1a−c. The contacts/feedthroughs in the illustration are not representative of all different practices reported in the literature, and they will be discussed in more detail in a separate subsection. Additional functionality, such as lead containment, can also be incorporated, as shown in Figure 1d.

3.2.1. Thin Film Encapsulation. Deposition of thin films to protect the devices is of significant interest for flexible and low-weight encapsulation. Therefore, this type of encapsulation would be highly desirable,[6] provided that it can yield satisfactory performance. In the published PSC literature,

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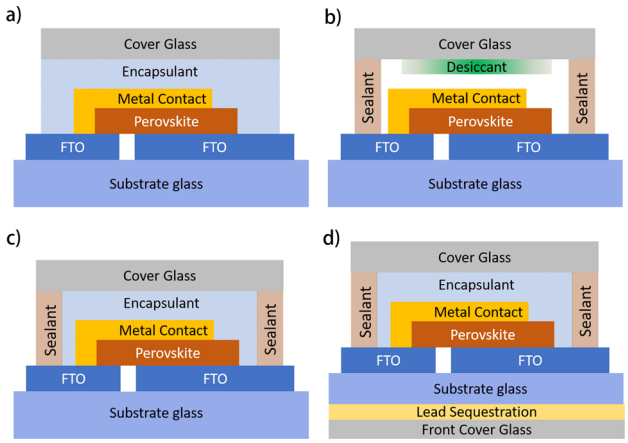

Figure 1. Schematic illustration of different types of cover glass encapsulation. (a) Blanket encapsulation, (b) edge encapsulation, (c) blanket encapsulation with edge sealing, and (d) sealed edge blanket encapsulation with added feature of lead containment. Note that in all cases the metal does not extend outside of the encapsulated area.

thin film encapsulation is often investigated for devices on rigid substrates, and it should also be noted that this type of encapsulation has not been used as a standalone in commercial PV technologies. Thin film encapsulation can include the interlayers and passivations incorporated as a part of the device structure[65,66] or the deposition of encapsulation layers on top of the device, which is what we will mainly consider in this section. The materials used for thin film encapsulation can include polymers as well as inorganic thin films.

Polymer films represent a simple encapsulation method which can be deposited by simple, low cost methods. However, a possible concern in polymer encapsulation is the solvent used for polymer coating, since it has been reported that poly(methyl methacrylate) (PMMA) deposition from chlorobenzene solutions can result in damage to the 2,2',7,7'-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiroOMeTAD) layer.[67] Various polymers have been reported for the encapsulation of perovskite films and devices, such as PDMS,[68] plasma polymer film from adamantane precursor,[69] poly(methylmethacrylate) (PMMA),[67,70−73] parylene C,[72] TPU,[74] PMMA/vulcanized silicone rubber,[75] PMMA//styrene-butadiene (SB),[76] fluoropolymer coating,[47] etc. In addition to polymer films, roll-transferred graphene has also been used[77] as well as spray-coated reduced graphene oxide (rGO).[9] Furthermore, other materials, such as hBN flakes and polycarbonate, have been used for encapsulation of perovskite materials,[78] but they have not been common in devices.

Inorganic films, such as silica or alumina, have also been used. Different from polymers, these films are typically deposited by various low pressure deposition methods, such as atomic layer deposition (ALD), sputtering, evaporation, etc. ALD deposited films, which could be encapsulation only[52,53,79] or incorporated as a part of the electrode,[80] have also been reported. ALD deposited films can also be combined with other films to form a barrier multilayer for enhanced encapsulation properties.[81,82] For example, combining the ALD coated alumina film with a hydrophobic surface modification with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane has also been shown to enhance the barrier performance against moisture ingress.[62] In addition to ALD, e-beam evaporation[51,83] and RF sputtering[84] have been used for depositing protective inorganic thin films, while plasma enhanced chemical vapor deposition (PECVD) has been used for depositing CF film encapsulation.[85] Air brush coating of hydrophobic zirconia films (several microns thick) was also reported.[63]

However, the use of thin film encapsulation for stability testing under harsh conditions has been scarce. For example, polymer layer-encapsulated PSC stability has typically been tested under mild conditions, such as ambient storage.[68,70,72] When damp heat testing is reported, it is typically performed for a short time, such as 1[75] and 100 h.[76] An exception is fluoropolymer coating (on top of the perovskite and back surface of the glass), where the devices were subject to outdoor testing in addition to exposure to high humidity (95%) environments,[47] and ∼500 nm thick spray-coated reduced graphene oxide (rGO) film encapsulation, where the devices were subjected to damp heat testing.[9] The situation is similar for inorganic thin film encapsulation, where the majority of reports show stability for ambient storage[80] with some exceptions reporting nonstandard accelerated aging conditions (shelf life at 50 °C, 50% RH)[81] and rarely considering harsh testing conditions, such as damp heat 85 °C, 85%RH[62] and outdoor testing.[63] Nevertheless, it is likely that thin film encapsulation combined with the cover glass/cover sheet encapsulation[51,76] can yield significantly improved performance. Out of the materials reported, the most promising ones when taking into account performance as well as the simplicity and low cost of the deposition are fluoropolymers[47] and spray coated rGO.[9] However, in the case of rGO, one possible problem is that the encapsulating film is expected to have low electrical resistance.

3.2.2. Cover Glass Encapsulation. Cover glass encapsulation has an advantage of the device being sandwiched between two moisture impermeable surfaces, which reduces the available area for moisture ingress to the sealant between the substrate and cover glass. Thus, this type of encapsulation generally offers superior performance compared to thin film or flexible plastic encapsulation,[67] although suitable selection of sealant is essential to ensure good lifetime. The use of various polymer materials instead of cover glass, including simple Kapton tape,[49] with or without inclusion of nanomaterial to reduce WVTR, combined with UV curable adhesive has also been reported in the literature,[55,67,86] but this type of encapsulation has not been subjected to rigorous testing protocols, such as damp heat testing. Polymer cover materials are primarily of interest for flexible PSCs (for a detailed review of various barrier materials and encapsulation strategies applicable to flexible devices, see ref.[7]), which generally do not exhibit good stability under damp heat and/or outdoor testing and thus we will mostly confine our discussion to devices on rigid substrates. Nevertheless, it is worthwhile to mention that ultimately suitable solutions need to be found for flexible devices due to their obvious advantages in reducing fabrication costs. Furthermore, additional features can be introduced when polymeric materials are used for encapsulation which can be beneficial for device performance. For example, the use of UV curable optical adhesive also enables the possibility of using micropatterning to increase the water contact angle, and such micropatterned surfaces can also be used on the substrate to decrease reflection losses.[86] Additional features which can be incorporated include the inclusion of a phase change material, such as poly(ethylene glycol) (PEG), into the resin to improve thermal management of the device,

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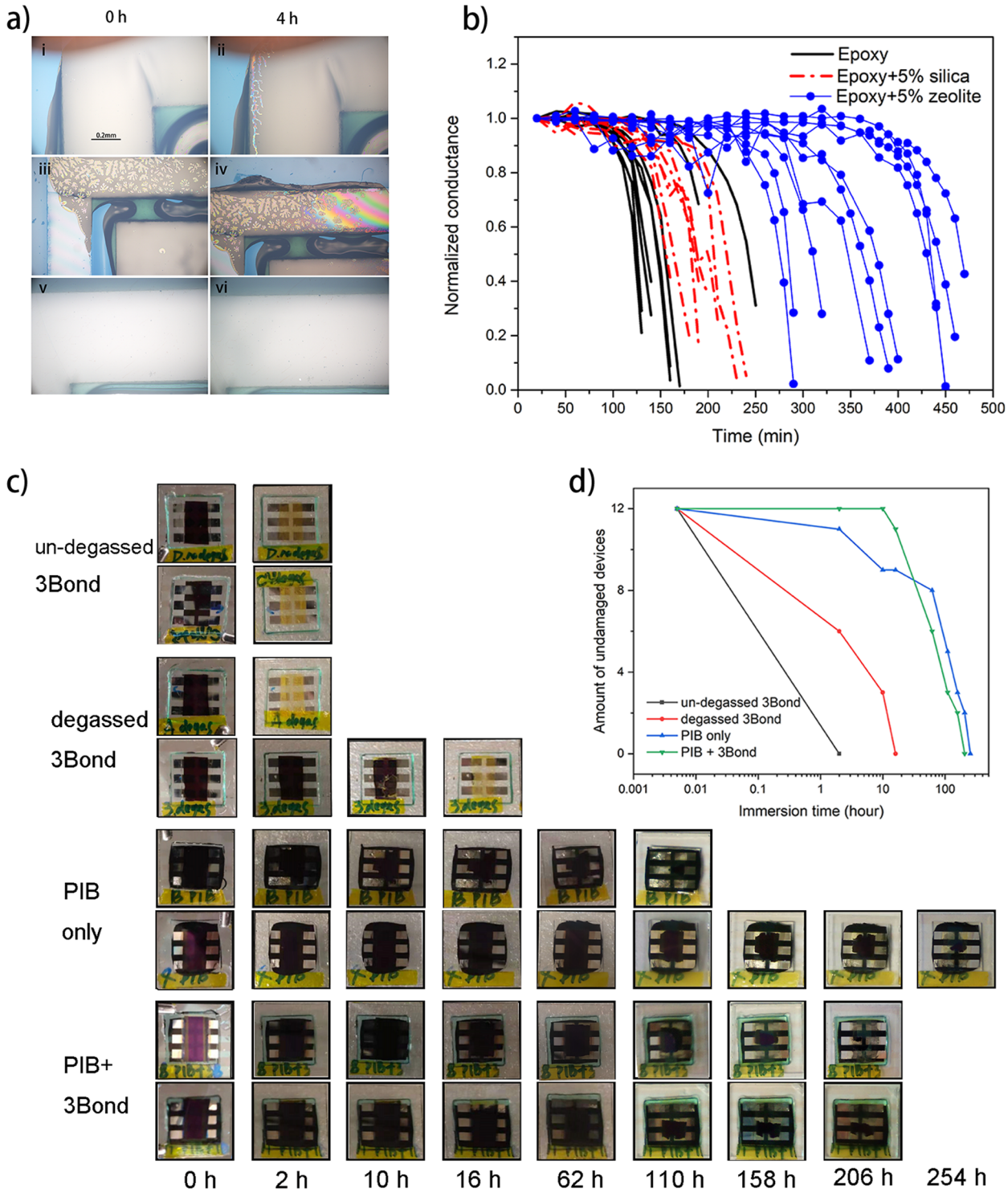

Figure 2. (a) Photos illustrating the formation of bubbles/delamination for Threebond UV curable epoxy before and after heating in ambient for 4 h. Left, epoxy cured with two pieces of glass held tightly together; middle, cured without pressing the cover glass and substrate together; right, with pressure during curing and with PIB. (b) Ca test for Threebond UV curable epoxy with and without incorporation of nanomaterials. (c) Photos of inverted perovskite solar cells encapsulated with different methods immersed into water heated at 85 °C. (d) number of working devices vs time for different encapsulation methods.

which in turn results in prolonged lifetime.[87] In addition, the encapsulation of flexible devices can include some unusual solutions such as sealing a flexible devices inside a cylindrical glass tube.[88]

The sealant with blanket coverage and/or edge sealing can be used to encapsulate the devices, as shown in Figure 1a–c. In addition, different forms of cover glass can be used, such as flat cover glass or cover glass with recess for placing the desiccant sheet for extending the lifetime of the packaged devices.[60] The inclusion of a desiccant or a combination of thin film encapsulation and cover glass encapsulation with desiccant has been shown to improve the stability of the devices.[51]

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However, the inclusion of glovebox atmosphere gases, which is unavoidable with recessed cover glass design, may result in the formation of bubbles in the epoxy and ultimately delamination, which in turn would have a negative effect on the device lifetime. All three approaches (edge-only, blanket-only, and combination blanket+edge seal) have been applied to PSCs, with the edge-only approach resembling encapsulation used in OLED technology, while blanket+edge sealing resembles other PV technologies. Direct comparisons between these approaches exists,[51,56,60] but they often include comparisons of different materials for different encapsulation approaches, and different testing protocols. Consequently, the obtained results have been somewhat contradictory and not necessarily generally applicable. For example, whether edge sealing or blanket sealing performs better is material dependent; i.e., it was reported that edge sealing results in better performance compared to blanket sealing for UV curable epoxy,[51] while in the case of PIB blanket sealing resulted in better performance.[56] In a more comprehensive examination of different types of encapsulation, comparing hot melt films, UV-curable and light-curable glue, and a combination of adhesive (Kapton polyimide) and UV-curable epoxy edge seal, it was found that the best performance is obtained in a combination of adhesive and UV curable edge seal.[89] This work included not only shelf life testing but also damp heat (nonstandard conditions), and while the obtained performance under damp heat was not impressive it should be noted that this is affected by both the intrinsic stability of the device and the quality of encapsulation. Also, it has been proposed that additional edge sealing could be detrimental for the performance of devices tested at high temperatures (over 80 °C) but it improves the performance for testing at lower temperatures.[61] However, it was also reported that when elevated temperature and humidity is combined with the illumination, edge sealing with a desiccant resulted in better performance compared to blanket sealing.[90] However, all the devices degraded relatively fast, and it is also uncertain whether this comparison would be generally valid or would depend on the encapsulant/sealant used.[90]

Despite the lack of consistent and comprehensive comparisons of encapsulation approaches across different studies, it clear that the presence of gas/void space in an encapsulation package resulting from edge-only sealing is associated with inferior thermal performance of the devices.[5] It was suggested that having a void space in the package is undesirable since it provides space for the escape of volatile products of the perovskite degradation.[12,56,91] It was also shown that PIB blanket coverage and cover glass encapsulation can significantly suppress the escape of volatile decomposition products, different from edge encapsulation.[12] However, it should be noted that exposure to high temperature (85 °C) can result in the formation of the bubbles in the UV curable edge seal even in the absence of perovskite, likely caused by thermal expansion of gas in the package resulting in delamination of the epoxy, as illustrated in Figure 2a. This phenomenon can be somewhat reduced by degassing of the epoxy before encapsulation, pressing the substrate and cover glasses together during UV curing, and optimized design of the cover glass package, and the phenomenon would likely depend on the mechanical properties of the edge seal material and its adhesion to glass. However, it is obvious that it cannot be completely eliminated as long as the encapsulated devices contain gas pockets (which also allow space for the perovskite volatile decomposition products), and thus, it is desirable to use blanket encapsulation or a combination of blanket encapsulation and edge sealing (reduction of this phenomenon with the use of PIB tape is illustrated) without leaving any gas space within encapsulation package. The disadvantage of edge only encapsulation containing the gas pockets is also illustrated by the test involving the immersion of devices into water kept at 85 °C, as shown in Figure 2c. The importance of degassing the epoxy is also obvious from the image, since the devices without degassing fail within the first 2 h (as obvious from the degradation of the dark perovskite to yellow PbI_2), while the devices can last up to 16 h in the case of degassed epoxy. In contrast, those encapsulated with PIB can survive over 200 h immersion in water at 85 °C (variation from substrate to substrate is due to manual encapsulation; if devices are encapsulated manually, increasing the number of substrates under test is highly advisable). It can be observed that the edge sealing with Threebond epoxy results in initially better performance (no degradation observed in all devices compared to reduced number of working devices for PIB only, since the devices start to fail from the edges toward the center once water penetrates the package), but eventually one substrate sealed with PIB only survived longer. It is expected that this would improve further with a different edge sealant exhibiting improved thermal/mechanical properties as well as a wider distance between the edge of encapsulation and the perovskite film.

Various edge sealants have been reported in the literature, including various UV curable epoxies and PIB. UV curable epoxies have the advantage of easy use at room temperature, but they tend to be brittle and result in cracks in testing conditions involving temperature cycling.[42] It is essential that the edge seal resists the ingress of moisture at high temperatures and that it can withstand temperature cycling without delamination.[42] Edge sealing around the wires used for electrical contact was reported to have a significant influence on the stability of flexible perovskite solar cells, and it should be used whenever there are bonded contact wires as part of the package.[92] Since the main purpose of the edge seal is to protect the devices from moisture, the performance of the edge seal material in general can be improved by incorporating a reactive desiccant, as demonstrated for a PIB edge sealant formulation with desiccant,[42,93] and we have also observed enhancements in outdoor lifetime upon incorporating a zeolite-based desiccant into a UV curable epoxy edge seal. In general, the use of composite materials for encapsulation is of interest to improve moisture resistance. For example, it has been shown that the incorporation of SiO_2 and graphene oxide can reduce WVTR for poly(vinyl alcohol-*co*-ethylene), which has been used to encapsulate PSCs with Norland optical adhesive edge seal.[55] In addition, improved moisture resistance demonstrated in a Ca test was achieved by mixing in nanomaterial (silica or zeolite) into a commercial UV curable epoxy is shown in Figure 2b (for more details on the Ca test and calculating WVTR, see ref 94). It should be noted that adding desiccant nanomaterials into commercial epoxy without desiccant will alter its viscosity. The viscosity and dispersion of the nanomaterial can be adjusted by using solvent additive, but this may alter epoxy properties. Nanomaterial desiccants which can be dispersed well (zeolite in the case of Threebond UV curable epoxy) will result in longer lag time and lower WVTR, compared to desiccants which are difficult to disperse uniformly within the epoxy. Furthermore, the ability of edge sealant to chemically binds to surfaces can also be beneficial for

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effective encapsulation, since it reduces delamination.[93] Finally, the width of the edge seal is important[12,40,42] for prolonging the lifetime (although at the expense of available device area), and devices exhibiting good performance in harsh stability tests typically have wide edge seals, 1 cm or more,[40,42] as expected based on the reported moisture diffusion with PIB edge seal.[20]

When it comes to the choice of encapsulant in blanket sealing, an important selection criterion is the lack of reactivity with the perovskite or other device components, due to direct contact between the encapsulant and the device. Not all materials are suitable for blanket coverage, and in some cases significant degradation of performance will occur with direct contact with the perovskite device, while for others there are no such issues.[51] Thus, one needs to consider encapsulant composition and curing methods, since the degradation of performance of encapsulated devices was observed with a thermally curable epoxy, which was attributed to outgassing during curing,[51] as well as Surlyn encapsulation.[95] However, the degradation of the performance after encapsulation or reaction between the epoxy and solar cell components has also been reported for UV curable epoxies,[60,94−96] with photoinitiators or polar components suggested to cause degradation.[96] Thus, it is important to carefully select the epoxy brand to be used for encapsulation and to apply it exactly as described in the literature report. Even for edge encapsulation, issues such as contact between the epoxy and the perovskite film can cause deterioration of the performance for some epoxy brands. In addition, some epoxies can exhibit undesirable reactions not only with the perovskite but also with organic charge transport layers in the device structure.[96] Nevertheless, the lifetime advantages of encapsulated devices over non-encapsulated ones are obvious, even with simple encapsulations using low cost glue (AB epoxy, Gorilla glue) and cover glass.[51,97] When using hot-melt films, it was found that in some cases (EVA and POE) worse performance was observed after encapsulation while polyurethane (PU) exhibited good performance.[48] However, it was also reported that polyolefins did not react with the perovskite, different from the case of EVA.[42] In general, EVA encapsulation may not necessarily be an optimal encapsulant due to acetic acid byproducts.[48,98] The possible damage to the device from the encapsulant before/during the curing could be prevented by coating the devices with a polymer film before cover glass encapsulation.[96] Polyvinylpyrrolidone (PVP) has been proposed as such a protective polymer layer,[96] and the use of other thin film encapsulations is also possible. For example, a combination of paraffin and UV curable epoxy has also been reported.[91]

Another important consideration for the choice of sealant is the mechanical properties, which are relevant for temperature cycling.[12,13,40,42,56,91,99,100] For example, EVA was found to exhibit better performance than Surlyn in thermal cycling tests due to its lower modulus.[13,40,42] Surlyn also resulted in inferior performance in lifetime tests under illumination compared to an epoxy sealant.[67] The importance of a low elastic modulus for temperature cycling and/or damp heat tests was also confirmed for different polyolefin encapsulants.[42] Finally, not only does the chosen material matter but also the thickness of the encapsulation determines how fast the perovskite will degrade.[101]

Since the devices sealed with only blanket encapsulation without edge sealing will exhibit degradation starting from the edges, cover glass encapsulation using adhesives covering the entire active area combined with some type of an edge seal is likely the best type of encapsulation for PSCs to achieve long-term stable performance, as expected based on the existing commercial PV encapsulation and distinctly different purposes of encapsulant and edge seal. Among different materials for encapsulation, PIB tape is rather straightforward and it has been demonstrated not to damage the perovskite film and to be suitable for damp heat tests[12,41] and outdoor tests.[41] When PIB blanket encapsulation is used, the best performance results can be expected using a vacuum laminator for a hot-press process, as described in ref 12. In the absence of such equipment, it is still possible to achieve effective encapsulation using PIB tape manually as described below. The PIB commonly used for encapsulation of photovoltaics from H.B. Fuller | KÖMMERLING (PVS101) is supplied as a tape with various tape dimensions, and the same company offers encapsulants in addition to edge sealants. Another example of a company offering an edge sealant suitable for PSCs is Quanex.[46] In general, the PIB tape is cut into pieces of desired size and then placed at the center of the cover glass. The PIB/cover glass is placed at 110 °C under pressure for 5 min to ensure tight and uniform adhesion between the PIB and cover glass. The PIB cover glass is hot-pressed onto the perovskite solar cell and kept at a mild temperature (90−110 °C) for 2−3 min to complete the encapsulation, while additional pressure is applied to the whole structure to achieve a good hermetic sealing. Encapsulation using PIB is a feasible and quick approach to achieve a stable and durable encapsulation of both rigid and flexible perovskite based devices against ambient air, and it represents a significant improvement over the use of epoxies. However, as discussed concerning encapsulation of established commercial PV technologies, it is necessary to achieve improved adhesion to ensure long lifetime under field conditions.

Finally, it should be noted that, in the choice of encapsulation method, one needs to take into consideration the purpose of encapsulation, i.e., whether the goal is to simply achieve as long lifetime as possible under the testing conditions or to perform any poststability testing investigations which require removal of the encapsulation. For hot-melt encapsulated samples, it was reported that encapsulation can be detached by heating to 100−130 °C.[48] Edge-sealed UV-epoxy encapsulated samples[51] can also be readily disassembled for follow-up investigations. PIB encapsulated samples, however, may present some difficulties due to strong adhesion between PIB and the perovskite device.

3.3. Other Relevant Encapsulation Details: Contacts, Desiccants, Additional Protective Layers, Lead Containment

In this section, we will briefly mention other, less common, encapsulation methods, followed by a discussion of additional details of encapsulation processes as well as the added functionality of lead containment. In addition to blanket and edge encapsulations and their combination, nonconventional encapsulation methods have also been reported, such as laminating two halves of the PSC.[102] However, this approach resulted in devices with low efficiency, and although stability upon water immersion for 24 h was reported, this only involved evaluation of device color while stability tests were performed for ambient storage.[102] Finally, other less common encapsulation methods, such as glass frit encapsulation,[99,100,103] should be mentioned. For this type of encapsulation, a laser is used to replace sintering of the glass

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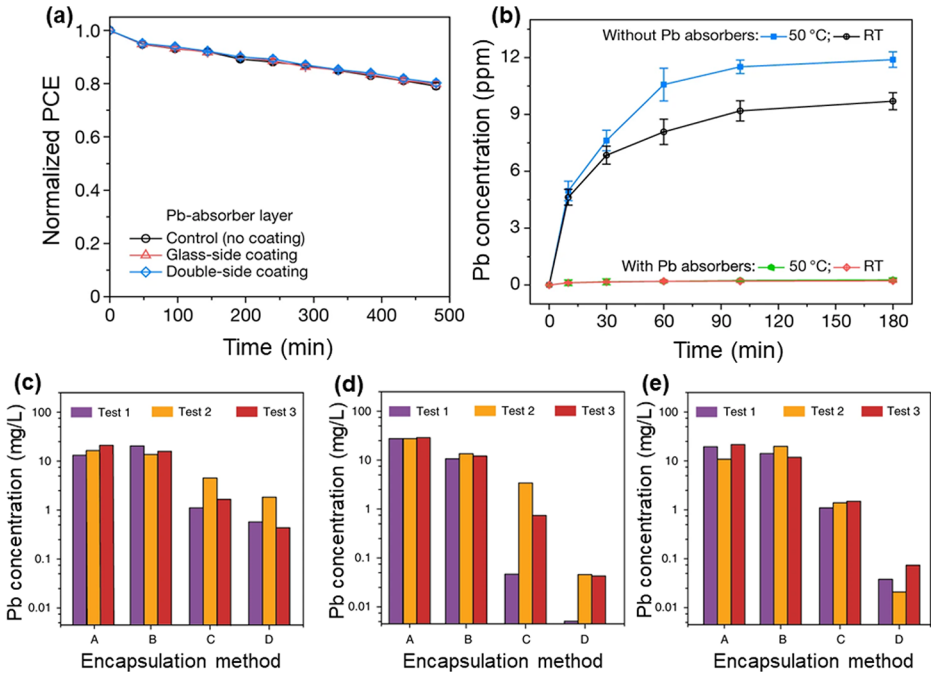

Figure 3. (a) Comparison of the *J*−*V* characteristics for PSCs prepared with and without the Pb-absorbing layers. (b) Pb-leaking measurement and comparison of the Pb sequestration for the damaged PSCs with and without the Pb-absorbing layers. Reprinted with permission from ref 106. The number of devices was 6. (c−e) Pb concentration in the contaminated water. Reprinted with permission from ref 104. (c) For experiment 1, water dripping tests were conducted on the damaged perovskite solar modules. The Pb concentration in the contaminated water was detected by ICP-MS measurements. (d) For experiment 2, the damaged perovskite solar modules were water dripped, heated at 45 °C for 4 h to simulate sunny weather, and then water dripped for the second time. The Pb concentration in the second dripping water was tested. (e) For experiment 3, the damaged perovskite solar modules were first heated at 45 °C for 4 h and then water dripped. The Pb concentration was tested. Three samples for each encapsulation methods were tested under each condition. The Pb leakage concentration is substantially influenced by the encapsulation methods.

frit and achieve hermetic sealing of the device.[103] While this method is extremely effective in preventing moisture ingress, it is more costly compared to other alternatives and it also does not address the issue of top electrode degradation by volatile perovskite decomposition products. It is well-known that the evaporation of HI resulting from the perovskite decomposition can corrode the top contact.[60] It was proposed that iodine sublimation could be minimized by covering the perovskite with impermeable layer to prevent iodine sublimation,[46] or alternatively nonmetal contact can be used.

Finally, an important feature of encapsulation is not only to prevent oxygen and moisture ingress into the package and thus ensure stable operation but also to prevent lead leakage into the environment.[5] It has been proposed that the use of self-healing epoxy resin-based polymers with a glass transition temperature around 42 °C between the perovskite device and the top glass cover can significantly reduce the leakage of lead.[104] The devices are effectively sandwiched between two cover glasses, using UV-curable epoxy and epoxy resin, and this type of encapsulation served to reduce lead leakage in case of mechanical damage simulating hail impact, as shown in Figure 3c−e.[104] The reduction of lead leakage was attributed to the self-healing of epoxy resin when exposed to temperatures higher than its glass transition temperature as expected during sunlight exposure.[104] It should be noted that the device temperature during outdoor operation can reach significantly higher temperatures than 42 °C (estimated temperature of ∼70 °C[48,105]) and significantly lower temperatures at night, and thus careful design of the polymer for a suitable glass transition temperature or an alternative approach (such as self-healing on ambient exposure instead of temperature mediated) is needed.

Another approach for lead sequestration involves coating the substrate glass with transparent lead-binding film (*P*,*P*'-di(2-ethylhexyl)methanediphosphonic acid) and coating the device stack on the metal side with the predried polymer composite film containing a lead-chelating agent (*N*,*N*,*N*',*N*'-ethyl enediaminetetrakis(methylenephosphonic acid) or EDTMP) in a polymer matrix (poly(ethylene oxide)), with EVA applied on the top surface.[106] This method has been shown to effectively reduce lead leakage from devices subjected to mechanical damage even at elevated temperatures (50 °C), and the coating was found to have no significant effect on the operational stability, as shown in Figure 3a and b.[106] However, it should be noted that the devices exhibited some degradation of performance, and thus, integration of lead-adsorbing components with more effective encapsulation approach would be highly desirable (as well as applying it to devices exhibiting improved stability compared to standard titania/3D mixed cation perovskite/2,2',7,7'-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD)/Au devices). Successful containment of lead was also demonstrated for an iron (III) benzene tricarboxylic acid (FeBTC)/poly(dopamine) (PDA) metal−organic framework (MOF) polymer composite, which could reduce lead concentration from a fully dissolved large area PSC to below the drinking water limit of the Environmental Protection Agency (EPA).[107] In addition, it has been demonstrated that diammonium phosphate (DAP) does not react with methyl ammonium lead iodide (MAPI) in a dry environment but in a humid environment results in the formation of water-insoluble

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Pb_2PO_4I, and that sensitive photodetectors based on DAP:MAPI mixture can be prepared.[108]

When it comes to good performance, not only the material choice but also the experimental details of the encapsulation process are important. In general, the performance of an encapsulation material is generally extrapolated to expected lifetime figures assuming an ideal case with no bubbles and no delamination.[93] However, bubbles can have a significant negative effect on the encapsulation effectiveness. It is important to follow the proper procedures for storing, handling, and applying encapsulation materials. For example, when using commercial barrier encapsulant films, it is important to follow appropriate conditioning procedures, which may include vacuum drying.[92] Other commercial supplies, such as desiccant sheets, are commonly packed in an inert atmosphere and should be kept in a glovebox. However, it should be noted that prolonged glovebox storage of an opened package of desiccant can result in inferior performance since the desiccant may also adsorb some of the solvent vapor present. In addition to using commercial desiccant sheets,[51] desiccants can be deposited on the surface of the cover glass or incorporated into the sealant material.[42,90,93] In addition, various films could be deposited on the surface of the perovskite for additional protection before encapsulation with the cover glass, such as SiO_2.[51] Different thin films could be used for this purpose (many of the examples listed in thin film encapsulation would be suitable choices), depending on the materials and deposition equipment available and taking into account minimizing the sample transfer between different pieces of equipment since this may contribute to increased exposure to dust and increased rates of device failure, as observed in tandem solar cells requiring transfer between multiple pieces of equipment.[109]

Another important detail of the encapsulation is the contact, namely, the use of ITO/metal contacts.[42,56] Improvement in the performance is observed when the metal contact does not extend outside of the packaged area of the device, i.e., when conductive oxide is used to make contact across the edge seal, since the extension of metal outside of the package can result in metal corrosion.[56] However, this can result in a decrease in device efficiency (mainly a drop in fill factor) due to sheet resistance of conductive oxide. Thus, contact pad design and electrical contacts to the device need to be optimized to minimize this issue, for example, by depositing contact pads outside of the encapsulated area over the ITO (separate metal electrode coated on top of ITO inside and outside of the package) and minimizing the ITO area connecting the top metal contact inside the package with metal contact pad outside of the package.

For an ideal encapsulation, the entire active area of the perovskite solar cell is blanketed by the encapsulant (such as PIB tape)/cover. If a different encapsulant from PIB tape is used, the PIB edge seal needs to be applied. A clean, metal, and residue-free surface outside the active area is required to achieve optimal adhesion of the PIB to the substrate to prevent gas penetration through the interface. In addition, since metal does not directly extend outside the area covered by the PIB, both the positive and negative contacts are realized through the conductive metal oxide (ITO/FTO) thin layer on the substrate, where additional metal contact pads can be deposited to reduce contact resistance. Therefore, precise patterning of the conductive metal oxide thin layer on the substrates is required prior to the fabrication of the active layers. Upon deposition of each active layer, the edge cleaning is performed respectively to thoroughly remove the residue on the edge area. Removing the device layers outside of the area within the encapsulation package is essential for achieving good stability. To achieve this, the solvent used for edge cleaning of each layer needs to be carefully selected while taking into consideration the physical and chemical properties of the corresponding materials. Solvents reported in the literature involve ethanol for the removal of the metal oxide before sintering and an isopropanol/DMSO mixture (20:1) for the removal of the perovskite and hole transport layer.[12] However, it should be noted that exposure to solvent vapor has a detrimental effect on the perovskite layer, leading to reduced device efficiency and stability. To minimize solvent exposure, an alternative procedure for cleaning the edge of the perovskite active layer involves removing the edge area mechanically using a blade, followed by wiping with minimum amount of methanol, which has a considerably high solubility for perovskite as well as a low boiling point. The wiping process should be performed rapidly while avoiding direct contact of the solvent to the perovskite layer. Using a small piece of a folded dust-free paper wipe rather than cotton/Q tip saturated with solvent is recommended since it can produce sharper edges and better results due to smaller amount of solvent vapor in the vicinity of the perovskite device which can either cause damage to the organic charge transport layers or cause changes in the perovskite crystallinity. The wiping process is then followed by annealing of the device substrate at 80 °C for 3 min to completely remove the solvent residue. If the device contains layers for which the edge removal procedure is not known, it is necessary to optimize edge removal by comparing the performance of encapsulated and nonencapsulated devices.

4. EVALUATING ENCAPSULATION

Stability testing of the encapsulated solar cells naturally includes evaluation of both device stability and suitability of encapsulation, and it is generally not possible to decouple the two contributing processes to device performance degradation. In the next section, we will briefly summarize relevant stability tests and discuss in detail those tests which have been less common due to harsh testing conditions (outdoor tests, damp heat tests). Since device degradation, including the degradation of encapsulated devices,[12] has been discussed in numerous reviews on device stability[1,110] as well as in some reviews on encapsulation,[8] we will not cover those issues in this Perspective. We will also not discuss basic materials characterization techniques such as optical microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, UV−vis spectroscopy, thermogravimmetric analysis, etc., which can be used to evaluate changes in encapsulation and/or devices with aging.[8]

Instead, we will discuss a specific issue for evaluating encapsulation, namely determination of the water WVTR using calcium tests.[94] WVTR can also be measured using commercial tools,[19,111] using the relative humidity sensor method ASTM 07 191[112] and FTIR method,[112] but Ca tests[94,111] remain common in the literature. For details of Ca tests, including both optical and electrical evaluations of WVTR, see ref 94. However, it should be noted that Ca tests are typically conducted in ambient indoor conditions to determine WVTR and that additional issues related to delamination (due to poor adhesion of material used or inadequate edge cleaning of PSC) may occur when the actual devices are subjected to testing, in

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particular in tests involving elevated temperature, such as damp heat tests (with very few exceptions[56]) or tests involving temperature cycling. In addition, an important consideration when conducting Ca tests is that some encapsulation materials may react with Ca while others react with layers in PSCs, which further complicates the evaluation of encapsulation for PSC applications.[94] Furthermore, while WVTRs of different permeation barriers for encapsulation of flexible devices have been determined, including different handling conditions (drying, applying pressure, using adhesion promoting layers), the difference in handling procedures was found to introduce significant differences (2−3 orders of magnitude) in WVTR, which would obviously affect the lifetime of the encapsulated devices.[94] The importance of small details in the process, which are not commonly mentioned in the Methods sections of papers, makes it difficult to replicate effective encapsulation despite promising results reported in the literature. Since the stability tests tend to be time-consuming, it is highly desirable to consider simpler and faster methods of establishing whether the encapsulation is good enough to likely yield sufficient device lifetime under standard stability testing protocols. For that purpose, it is worthwhile to mention possible methods for testing the effectiveness of encapsulation in addition to determining WVTR.

For example, monitoring the perovskite film degradation has been previously proposed as a means for simple testing of encapsulation, but this technique has a drawback that the method which provides good protection of the perovskite film does not necessarily result in good performance of an entire PSC.[67] Similarly, an alternative test for encapsulation using the optical properties of perovskite films subjected to damp heat aging has also been proposed.[101] However, this test would likely not directly translate to good device performance under damp heat testing conditions since it is not uncommon that degraded devices still exhibit the dark color of the perovskite after the efficiency has dropped significantly, with the main cause of failure being the degradation of the interfaces and metal electrode due to ion migration rather than the decomposition of the perovskite. Other nonconventional tests involve water immersion for varying periods of time,[49,62,69,74,77,102,113−115] from 1 min[69] to 4 days,[74] and annealing at higher temperatures compared to standard tests.[49] A stability test with placing water on encapsulated surface of a PSC was also reported,[55,86] and the results were strongly dependent on the type of encapsulation.

Another possible method to accelerate the test of encapsulation used is to subject the devices to an even more extreme testing condition compared to intended testing. Such methods of rapid screening for encapsulation include higher temperature and humidity (120 °C, 100% RH) combined with UV illumination.[13,42] Another suggested method for further acceleration of testing is the pressure cooker test (105 °C, 85% RH), which allows a clear distinction in encapsulation reliability in less than 200 h compared to longer times needed for the damp heat (DH) test to observe differences among encapsulation approaches.[28] Another example of further acceleration of encapsulation testing is the immersion of devices into water heated to 85 °C, which is obviously more harsh than damp heat test. We have illustrated the results of such a test in Figure 2c, so that the effectiveness of encapsulation which can lead to excellent stability with >800 h of damp heat testing and over 1700 h of outdoor testing in a very humid climate can be verified in around 200 h. While this type of test is not included in the ISOS protocols for perovskite solar cell testing,[11] these and similar tests can be relevant for testing the quality of encapsulation, since subjecting the devices to much harsher conditions will result in faster failure and can translate to suitable long lifetimes under damp heat and/or outdoor testing.

5. DEVICE STABILITY TESTING

The standards for testing the solar cells include IEC TR 63 228:2019 for efficiency testing of emerging PV technologies[116] and IEC 61 215:2016 (now IEC 61 215:2021) for stability testing.[3,117] This includes combinations of rather harsh testing conditions, which are rarely implemented all together for perovskite solar cells. While these tests are essential for commercialization, for the advancement of research, it is necessary to observe standardized condition testing although these conditions do not necessarily need to be as rigorous. The perovskite community has been lagging behind the OPV community in standardized and/or interlaboratory testing, but there have been reports on multisite stability testing following different ISOS protocols.[59] ISOS protocols have been originally developed for standardized OPV testing,[10] and they have been recently updated for perovskites and the consensus statement on the stability testing of PSCs has been published.[11] These protocols are intended to ensure that the stability testing among different laboratories is comparable, and thus improve the quality and relevance of the published data.[11] This consensus statement outlines different testing protocols for testing in the dark, testing under light soaking, outdoor testing, thermal cycling, solar-thermal cycling, light cycling, and testing under bias, with the last two protocols being additions specific to PSCs.[11] Each of the testing protocols contains possible variations in the level of sophistication, such as open circuit or maximum power point (MPP) testing, with MPP being recommended for testing involving illumination. The open circuit (OC) condition has been reported to be a more harsh testing condition compared to MPP testing,[46] and it is known that the perovskite degradation is bias and morphology dependent.[118] Thus, performing MPP testing instead of OC testing not only would be in line with the recommendations, but also would likely result in longer achieved lifetime.

As mentioned, shelf life or dark storage testing is very common in studies of perovskite solar cells. However, even if devices exhibit a very long lifetime for storage at room temperature in the dark, the lifetime under illumination or elevated temperature or humidity is typically much shorter and also considerably more relevant. For example, even simple encapsulation using UV epoxy can result in stable performance of the devices with carbon-based electrodes for a period of 5 years of ambient exposure,[113] but the efficiency of such devices is commonly significantly lower compared to devices with metal electrodes. In addition, stable performance for 7500 h was reported for cells which exhibited T_{80} of less than 200 h when exposed to 85% RH at 65 °C.[53] In general, the achievement of a long shelf life in PSCs is not too difficult with recent advances in the perovskite film and device architecture, while improvements in thermal stability and stability under illumination are more difficult to achieve. Thus, as a relevant test of the device stability, it is necessary to consider not only exposing the device to the ambient conditions, but rather exposing the devices to environmental degradation factors (oxygen, humidity) combined with other stressors, such as light, elevated temperature, and/or bias. Considering the

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factors contributing to the degradation of PSCs, the most informative test combination would be one of the tests involving illumination, such as ISOS-L, ISOS-LC, ISOS-O, or ISOS-LT protocols, combined with one of the tests involving an 85 °C temperature (to account for the fact that temperatures during outdoor operation are expected to exceed 65 °C), such as ISOS-D3, ISOS-V3, or ISOS-T protocols.

Testing the stability of perovskite films and devices under illumination in ambient conditions is exceedingly important, since the solar cells must function under illumination while the perovskite materials and devices are susceptible to unique degradation processes under these conditions.[11,119] Since increased humidity significantly accelerates the degradation,[90] numerous efforts have been devoted to improve the stability of the devices upon exposure to humidity while other degradation processes, such as photoinduced degradation in the presence of oxygen[120] have been getting comparatively less attention. However, it has been noted that the accelerated aging under constant illumination does not necessarily represent a realistic estimate of perovskite stability due to differences between such testing conditions and actual outdoor testing.[121] Outdoor testing or at least testing involving light-dark cycling is important because PSCs exhibit both reversible (recovery in the dark) and irreversible degradation.[122] Since the cells can exhibit both reversible degradation and reversible improvements with diurnal cycles, it has been proposed that a more suitable measure of stable performance should be the time it takes for the power generated in the first day of testing to reduce by 20%, instead of commonly considered T_{80} value, i.e., time for initial efficiency to be reduced by 20%.[123] In addition to the performance variation during light/dark cycles, temperature variation in outdoor testing is another important parameter which affects device stability.[121,124] It should also be noted that the significance of the effects of temperature variation and light/dark cycles as opposed to testing under constant illumination and at constant temperature depends on the actual device architecture.[121,124] Another point to note is that under constant illumination PSCs can exhibit a "burn-in" phase,[125] so the determined T_{90} or T_{80} can differ depending on whether the burn-in part of the testing is taken into account or the initial value is taken to be the efficiency after the cells are stabilized after the burn-in phase. Some devices also exhibit an increase in the efficiency after illumination, followed by degradation which also complicates the determination of T_{80}.[11] Thus, the stabilized T_{80} value T_{S80} can be considered as a figure of merit in reporting the stability of devices with such pronounced variation in early part of the stability test. Among various testing protocols incorporating illumination, we will focus on outdoor testing reports as the most relevant for practical applications.

In addition to degradation under illumination, degradation with exposure to elevated temperatures is another critical factor which needs to be evaluated in testing the stability of PSCs. Here we will mainly focus on discussing the damp heat tests, because they combine exposure to high humidity with exposure to high temperature and outdoor tests as tests under illumination. The combination of damp heat testing (high temperature, high humidity) and outdoor testing (illumination cycling, temperature cycling, weather variations) covers the majority of stressors affecting the device stability. We will not discuss in detail the thermal cycling tests, since they typically do not incorporate high humidity or light exposure (exception are ISOS-LT protocols which have been scarce) which significantly accelerates PSC degradation, but we would like to point out that they do have relevance for outdoor performance due to temperature variations throughout the day. Thus, for cells to successfully function outdoors for prolonged lifetimes, it is desirable to use encapsulation materials with suitable mechanical properties, i.e., encapsulants capable of dissipating the strain.[13] It should also be noted that the temperatures of perovskite cells and modules operating in outdoor conditions have been estimated to be able to reach 70 °C[48,105] and, in general, thermal management of perovskite devices can be challenging since metal halide perovskite materials have very low thermal conductivity[126] and devices are typically deposited on glass and encapsulated with glass cover which leads to heat accumulation.[76] High operating temperatures under outdoor conditions are also highly relevant for Si/perovskite tandem cells, where a different optimal composition of the perovskite needs to be chosen to achieve stable performance due to the need for mixed perovskite layers with improved thermal stability.[64]

Reports on both damp heat testing and outdoor testing for PSCs have been scarce, since achieving good stability under these conditions is nontrivial and requires not only effective encapsulation but also devices with excellent intrinsic stability. The device architecture plays a significant role in intrinsic stability, since the encapsulation is not going to address the effects of ion migration which are a significant contributor to the degradation of the device performance, and the degradation of encapsulated devices was found to occur due to ion migration and interface deterioration.[127,128] For a detailed review of possible ways to improve device intrinsic device stability, see ref 128. Here we will just highlight several issues which were found to significantly affect stability under harsh testing conditions. For example, it has been pointed out that in order to pass the damp heat tests, UV exposure test, and thermal cycling test, TiO_2 should be eliminated to improve stability upon UV exposure and ITO needs to be deposited below the Ag electrode to prevent moisture ingress into the device and the escape of volatile degradation products from the perovskite layer and their reaction with the electrode.[13] Other suggestions include eliminating metal electrodes and eliminating methylammonium from the perovskite layer.[129] However, it has been reported that even devices without metal electrodes, namely, carbon-based PSCs, can exhibit poor thermal stability when heated to 80 °C although they remain stable at temperatures 50 °C and below.[130] Furthermore, devices containing Cs were found to have improved thermal stability compared to devices without Cs, resulting in lower emission of volatile decomposition products.[12] It has also been shown that the insertion of interfacial layers for hindering ion migration is highly beneficial for achieving good device stability, as demonstrated for devices using a 3D/2D perovskite and subphthalocyanine based interfacial layer.[41] For conventional architectures, a good combination of charge transport and interfacial layers involves thermally stable organics (P3HT:CuPc) combined with metal oxides (IZO).[43] Other suggestions include replacing the spiro-OMeTAD with a different, more stable hole transport layer or with an undoped hole transport layer that can also result in improved stability.[9,43,76,131,132] In addition to the replacement of spiro-OMeTAD, the replacement of MoO_x is needed for devices subjected to temperatures above 70 °C.[76] Vanadium oxide VO_x represents a possible replacement for MoO_x to improve high temperature stability.[133]

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Table 2. Reported Encapsulations and Performance Parameters for PSCs Subjected to Long Term Damp Heat Tests with Standard Test Conditions of 85% RH, 85°C (η Denotes Power Conversion Efficiency, η_0 Denotes Initial Efficiency)[a]

encapsulation	device type, architecture	η (%)	test time (h), T_{80} (h)	final η (%)	ref
EVA encapsulant, butyl rubber edge sealant	PSC, inverted	∼10−12	1000, >1000	12% (increase from 10%)	13
butyl rubber edge seal with desiccant, POE ENLIGHT encapsulant	PSC, inverted	∼11−13	1000, >1000	95% of η_0	42
glass frit encapsulation	PSC, conventional mesoscopic with C	8.2	50, >50	100.9% of η_0	99
no details given	PSC, inverted	14.76	600, >600	93.8% of η_0	135
double layer ALD alumina/hydrophobic coating	PSC, inverted	19.9	500, 500	80% of η_0	62
face sealing adhesive sheet	PSC, conventional	21.16	1070, >1070	93.9% of η_0	131
blanket PIB	PSC, conventional	∼7−9	540, >540	98% of η_0	56
blanket PIB	PSC, conventional	∼17−19	1800, >1800	100% of η_0	12
blanket PIB, UV curable epoxy edge seal	PSC, inverted	∼20	816, 816	80% of η_0	41
PIB edge sealing, cover glass	PSC, conventional	∼20	1000, >1000	91.7% of η_0	43
rGO film	PSC, conventional	–	1000, >1000	85% of η_0	9
face sealing OLED adhesive sheets	PSC, conventional	19.7	530, >530	89.3% of η_0	134
EVA, butyl rubber edge seal	PSC, inverted	∼10−12	1008, >1008	∼12%, increase from 10%	45
PMMA/SB	PSC, conventional	∼19	100 h, 100 h	80% of η_0	76

[a]Empty spaces in the table indicate that information was not provided, for example, T_{80} not given, or if the efficiency was given for different device configuration compared to long term stability test.

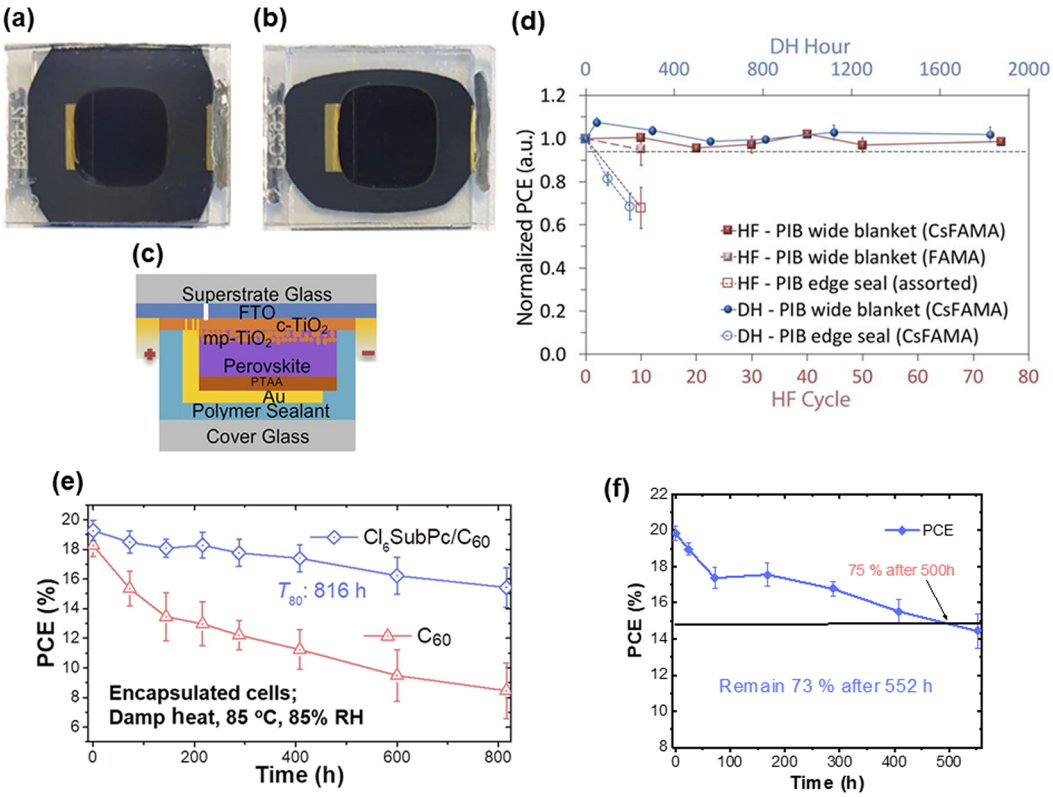

Figure 4. Solar cells for IEC 61 215:2016 damp heat and thermal cycling tests (a−d): (a) "Front" view (from the superstrate side) of PSC after PIB-based blanket encapsulation. (b) PO-based blanket encapsulation, (c) Illustrations of the cross sections of the respective encapsulation scheme. (d) PCE evolution of PIB-encapsulated or edge-sealed PSCs. Reprinted with permission from ref 12. The number of devices for different test conditions was 2−4. The damp heat test data correspond to 3 devices with wide blanket encapsulation and 4 devices with an edge seal. (e) Damp heat stability tests of the encapsulated control C60 devices (5 cells) and Cl_6SubPc/C60 devices (5 cells). Reprinted with permission from ref 41. (f) Damp heat stability tests with illumination for the devices with the same architecture as in panel (e) (5 devices).

5.1. Damp Heat Testing

Damp heat or ISOS-D3 tests have rarely been reported, but different types of PSCs have successfully passed several hundred hours of damp heat testing and even exceeded the requirement of 1000 h, as summarized in Table 2. The majority of the devices include conventional architecture devices. For example, cells consisting of FTO/TiO_2/FA-based perovskite/doped poly[bis(4-phenyl)(2,4,6- trimethylphenyl)-

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Table 3. Reported Encapsulations and Performance Parameters for PSCs Subjected to Long Term Outdoor Tests (η Denotes Power Conversion Efficiency, η_0 Denotes Initial Efficiency)[a]

encapsulation	device type, architecture	η (%)	test time, T_{80}	final η (%)	ref
butyl rubber edge sealant (Quanex), HelioSeal PVS 101 contact seal	Si/perovskite (inverted) tandem	~23	6 months, –	~45% of initial power density	46
ThreeBond edge sealant, SiO_2 film	PSC, conventional	14.8	432 h, –	~11	51
polyurethane	module, conventional mesoscopic with C	10	3 months, >3 months	97.52% of η_0	48
UV curable epoxy	PSC, conventional	~ 5–6	560 h, ~100 h	0	58
UV curable epoxy, glass, waterproof silicone	PSC, conventional mesoscopic with C	~5–9	30 days, over 30 days	no significant decrease	59
blanket PIB, UV curable epoxy edge seal	PSC, inverted	~20	1728 h, >1728 h	87% of η_0	41
fluoropolymer coating	PSC, conventional	~17	2160 h, 2160 h	95% of η_0	47
EVA	module, inverted	~6–12	800–2200 h, 80–1442 h	~55% initial power	44
epoxy, Surlyn, cover glass	PSC, conventional mesoscopic with C	12.9	7 days, >168 h	slight increase	50
Ossila, Encapsulation Epoxy E131	PSC, conventional	11.02	1008 h, 846 h	60% of η_0	57
glass, Pattex silicon	module, conventional mesoscopic with C	~ 8	30 days, >30 days	no significant change	138
hydrophobic zirconia film	PSC, conventional mesoscopic with C	~15–16	150 days, >150 days	no significant degradation	63
polyolefin, cover glass	Si/perovskite (inverted) tandem	25.1	1 week, –	–	64
two component resin edge encapsulation	PSC, inverted	18.5%	111 days, 35 days T_{50}	–	136
PMMA/SB, Al sheet	PSC, conventional	~19	500 h, 500 h	90% of η_0	76

[a]Empty spaces in the table indicate that information was not provided, for example, T_{80} not given, or if the efficiency was given for different device configuration compared to long term stability test.

amine] (PTAA)/Au devices sealed with PIB blanket encapsulation and with an efficiency of ~8.5% exhibited excellent stability during 540 h of damp heat testing.[56] The longest reported time for damp heat testing involves PIB blanket-encapsulated cells with a conventional architecture, as shown in Figure 4a–c, which exhibited negligible degradation during 1800 h of damp heat testing and also exhibited excellent performance in humidity-freeze tests, as shown in Figure 4d.[12] Thus, these devices exceeded by a significant margin the minimum requirement to pass an IEC 61 215:2016 standard test (1000 h).[12] It should be noted that only wide PIB blanket coverage results in devices capable of passing damp heat tests and a polyolefin-based narrow blanket as well as PIB edge encapsulation failed to deliver acceptable performance.[12] However, it should be noted that these devices exhibited degradation during MPP testing when the temperature increased to 45 °C even during a short testing time.[12] Other device architectures which successfully passed the damp heat test include ITO/c-TiO_2/TiO_2 nanorods/PMMA:PCBM/$Cs_{0.05}FA_{0.88}MA_{0.07}$ $PbI_{2.56}Br_{0.44}$/PMMA/P3HT:CuPc/MoO_x (~10 nm)/IZO (~40 nm)/gold,[43] where the barrier layers below the gold electrode were identified as critical for passing the damp heat test. Interfacial modification between the perovskite and hole transport layer has also been shown to improve device stability.[134]

The simple inverted devices with the architecture ITO/NiO/$CH_3NH_3PbI_3$/PCBM/Ag encapsulated by a hydrophobic composite bilayer have been reported to exhibit around 80% of initial efficiency after 500 h of damp heat test and 90% of initial efficiency after 1000 h of illumination, illustrating the excellent stability potential of inverted devices.[62] However, to improve this, it is necessary to address the degradation of the Ag electrode, which can be achieved either by replacing it with a more stable material or by incorporating interfacial layers to suppress ion migration. Damp heat testing was also reported for inverted devices with the architecture NiO_x/perovskite 3D/2D/boron chloride subphthalocyanine (Cl_6SubPc)/C60/BCP/Ag encapsulated with PIB and UV curable epoxy, and the obtained T_{80} was 816 h,[41] as shown in Figure 4e. While this is less than 1000 h required to pass the test (and it could likely be improved by using a wider PIB cover), the devices exhibited excellent stability under MPP tracking in the ambient environment, retaining 90% of the initial PCE after 2034 h.[41] However, the obtained T_{80} is significantly shorter when the damp heat test is combined with illumination, as shown in Figure 4f, and we can expect that the same trend would generally apply due to additional stress on the devices with added illumination.

Other inverted devices subjected to damp heat testing include the architecture glass/ITO/2-(3,6-dimethoxy-9*H*-carbazol-9-yl)ethyl] phosphonic acid (MeO-2PACz)/perovskite/C60/ SnO_2/Cu, where the presence of SnO_2 was introduced to improve the stability of the devices by protecting the electrode,[136] but these devices were encapsulated using edge encapsulation and the stability would likely be improved if encapsulation is optimized. On the other hand, devices with the architecture ITO/NiO_x/perovskite/LiF/PCBM/SnO_2/ZTO/ITO/Ag encapsulated using EVA and a butyl rubber edge seal exhibited good stability under 1008 h of damp heat testing.[45] Thus, we can conclude that devices with excellent thermal stability and minimized ion migration as well as the use of suitable encapsulation (appropriate choice of blanket encapsulant and edge seal) are necessary for good performance in a damp heat test.

5.2. Outdoor Testing

Reports on outdoor testing of perovskite solar cells have been scarce. The reported encapsulations for PSCs subjected to outdoor testing with sufficiently long test times are listed in Table 3.[41,44,46,47,51,57−59,64,137,138] Nevertheless, existing reports include perovskite cells and modules as well as perovskite tandem devices, and the tests were conducted in a variety of

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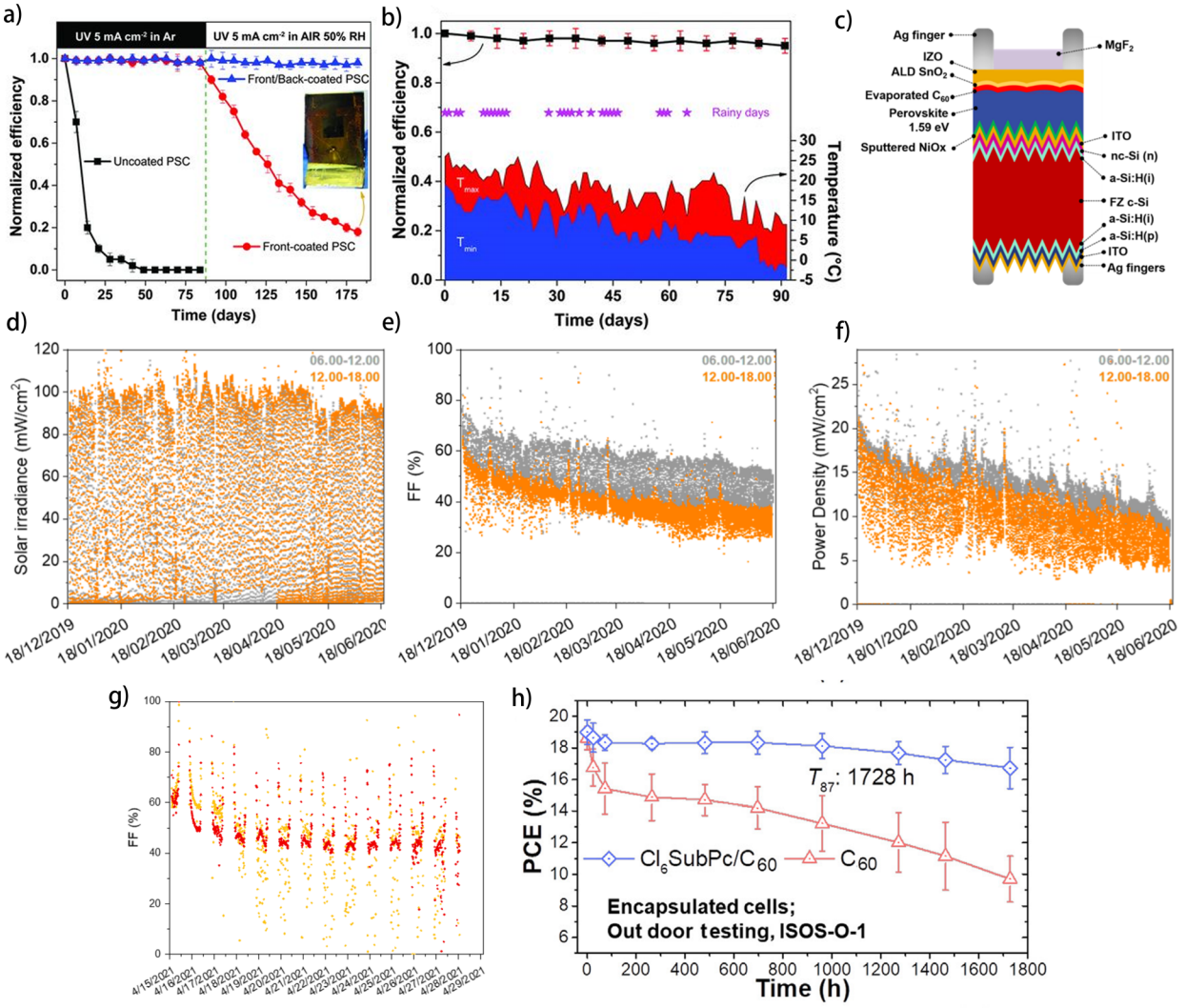

Figure 5. (a,b) Aging of LDS-PSC integrated system: (a) Results of the aging test on the three series of PSCs: uncoated, front-coated (i.e., luminescent fluorinated coating on the front side), and front/back-coated (i.e., front side coated with the luminescent fluorophore and back contact coated with the moisture-resistant fluoropolymeric layer). During the first 3 months, PSCs were kept under Ar atmosphere, and in the next 3 months under air at 50% RH, with both cases under continuous UV irradiation. PCE was measured once a week. A digital photograph of a front-coated solar cell at the end of the test is also shown. (b) Results of the aging test on front/back-coated devices left for 3 months on the terrace of the Politecnico di Torino building in Turin (Italy), thus experiencing real outdoor operating conditions. Reprinted with permission from ref 47. The number of devices was 5. (c–g) Outdoor performance of perovskite/silicon tandem devices: (c) Bifacial monolithic tandem layout. (d) Solar irradiance measured in the outdoor test-field from November 19, 2019 to June 17, 2020, (e,f) FF and the power density of sample A, over 6 months. Morning data (06:00–12:00) are highlighted in gray, while the afternoon data (12:00–18:00) are in orange. (g) FF variation on single junction perovskite solar cells in the test-field. Test-field location: Jeddah, Saudi Arabia (22.302 494, 39.110 737). Reprinted with permission from ref 46. Copyright 2021 American Chemical Society. (h) Outdoor stability tests of the encapsulated control C60 devices (5 cells) and Cl_6SubPc/C60 devices (9 cells) following the ISOS-O-1 protocol standard. Reprinted with permission from ref 41.

locations, such as Barcelona, Spain[57,59] and Paola, Malta;[59] Turin, Italy;[47] Medellin, Colombia;[44,137] Jeddah, Saudi Arabia;[46,50,64] Ljubljana, Slovenia;[136,139] New Delhi, India;[58] Laiyuan County,[48] Wuhan,[138] and Hong Kong, China.[41,51] The outdoor performance has been investigated for a range of temperatures, humidities, and irradiances,[137] and testing protocols involve both ISOS-O1 (open circuit or MPP tracking) and ISOS-O2. The open circuit testing is straightforward but it will likely result in an underestimation of device lifetime compared to MPP testing, but for both testing protocols inherent light/dark cycling in outdoor testing would result in some recovery of the efficiency during the night. It is also important to note that the humidity and temperature ranges are location dependent but there is a general expectation that surface temperatures of the devices will significantly exceed the ambient temperatures. For example, it was reported that the surface temperature of the module can reach up to 70 °C[48,105] for outdoor temperatures in the range from −10 to 35 °C.[48]

The outdoor stability tests are most commonly reported for devices with conventional architecture, such as devices consisting of a TiO_2/ZrO_2C stack infiltrated with the perovskite (aminovaleric acid (AVA)-methylammonium lead iodide),[48,50,59,63,138] and a common perovskite architecture consisting of TiO_2/perovskite/spiro-OMeTAD/Au (mesoporous[47,57] and planar[51]). In comparison, inverted PSCs have been less commonly tested outdoors. The reported results include modules with the architecture (NiO_x/Al_2O_3/$MAPbI_3$/

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PCMB/rhodamine/Au[44,137] and cells with the architecture NiO_x/perovskite 3D/2D/boron chloride subphthalocyanine (Cl_6SubPc)/C60/BCP/Ag.[41] Among the individual PSCs, long lifetimes have been reported for both conventional devices (>2100 h),[47] as shown in Figure 5a and b, and inverted devices (>1700 h),[41] as shown in Figure 5h.

Among the longest reported outdoor test is the 6 month outdoor test of perovskite-silicon tandems, conducted in Jeddah, Saudi Arabia, also shown in Figure 5c–f.[46] The tandem cells exhibited degradation which was a combination of reversible degradation (recoverable overnight, attributed to ion migration) and irreversible degradation, due to Ag contact deterioration.[46] It should be noted that this contact degradation occurred despite the fact that Ag is separated from the perovskite layer by C60, ALD deposited SnO_2, and indium zinc oxide (IZO layer) and Ag fingers are laterally separated by MgF_2.[46] The degradation of the Ag electrode was attributed to the iodine sublimation, and suggested methods of improvement included the elimination of exposed perovskite layer and including two layers of encapsulant materials which can provide a barrier to iodine sublimation.[46]

5.3. Further Acceleration of Stability Testing: Nonstandard Accelerated Testing

In addition to the standard testing protocols, there is also a need for further acceleration of testing protocols, which may facilitate the change in stability investigations. Dark storage stability protocols likely remain the most popular for the following reasons: (a) they typically provide impressive numbers and there is no "failing" in the dark storage test for any reasonable cell; (b) they require a minimal investment of active researcher and equipment time (only for the periodic checks of PCE, as opposed to constant utilization of environmental chamber and/or solar simulator); and (c) a practically unlimited number of different devices from different ongoing projects can be stored at the same time. Other testing protocols which involve illumination or temperature and/or humidity control can result in poor results (or "failure" if the goal is to maintain a certain level of efficiency for a specific number of hours) and require constant the use of relevant equipment for the duration of the test. Since the number of solar simulators and/or environmental chambers is typically limited in a research lab, the devices are commonly tested sequentially. To illustrate the need for shorter testing times compared to standard testing protocols, let us consider the need to deliver devices which can pass the damp heat test (T_{80} > 1000 h) to fulfill a project objective. If one starts with a device which exhibits T_{80} of 504 h (3 weeks), and assuming optimistically that there are only two intermediate iterations (with corresponding T_{80} values of 4 and 5 weeks) needed to produce a device which exhibits T_{80} of 1008 h (6 weeks), the total time spent on stability testing only would be 18 weeks (~4.5 months). Such a significant time investment (even when not counting the time spent to actually develop more stable devices including exploring blind alleys where stability improvement has been achieved at the expense of lower PCE) obviously discourages the development of stable devices. Thus, if one can find out if the stability improvement has been achieved within days rather than weeks, the development of the improved stability devices can be accelerated considerably.

For example, for the purpose of accelerated testing to determine whether the devices are susceptible to ion migration, testing under bias is potentially of interest. The ISOS protocols propose testing under bias in the dark, with or without thermal stress.[11] However, adding illumination to the applied reverse bias can significantly accelerate degradation in devices susceptible to ion migration.[41] For a detailed discussion of the degradation processes under reverse bias, see ref 140. This is practically relevant, since cells in a module may operate under reverse bias due to partial shading,[140] and offers significant acceleration of the stability test, since much faster degradation, including deposition of the metal electrode on the substrate glass, can be observed when negative bias is applied to devices under illumination.[41] This degradation process can be significantly suppressed by inserting suitable interfacial layers which inhibit ion migration,[41] and thus, it can serve as a fast test of susceptibility to ion migration since the testing time can be shortened to several hours as opposed to hundreds of hours in common testing protocols. An alternative method to accelerate stability testing is to perform the tests at a higher light intensity, with significant acceleration of the degradation already achievable at 5 suns intensity.[11] While the use of such testing to obtain estimates of lifetimes under outdoor testing would be complex and requires making assumptions about the scaling of degradation processes, the use of enhanced acceleration tests can have a place in the development of devices with enhanced stability since it can significantly shorten the testing time.

6. OUTSTANDING ISSUES

It has been estimated that it is necessary to develop encapsulation materials with WVTR below 10^{-5} g/m^2 day to achieve stable PSCs,[94] which is obviously challenging. Thus, there is a need for further development of encapsulant, edge sealant, and/or barrier materials specific to perovskite devices with reduced processing temperature for encapsulation, reduced WVTR and OTR, improved adhesion, improved mechanical and thermal properties, and improved stability, and a lack of reactivity with perovskite layers or other device components is needed. In terms of the edge seal, investigation of dual seals where additional material is used to protect the PIB[24] is needed to address the issue that manufacturing defects in PIB result in rapid degradation in the ambient environment due to moisture diffusion through the breach in the PIB. Further development is also needed for flexible barrier materials, since the current state-of-the-art materials are still insufficient to achieve a 25 year lifetime.[7]

In addition to the basic feature of encapsulation to protect the device from exposure to ambient air, it is of interest to have added functionality due to unique issues relevant for halide perovskite materials. For example, among other features which need to be explored further is the incorporation of some form of thermal management into the encapsulation package. The proof of concept for thermal management has been reported,[87] but it needs to be refined and incorporated into more advanced encapsulation methods and rigorously tested under harsh testing conditions. It has been well documented that the temperature of the PSC module significantly exceeds outdoor temperatures and can reach 70 °C.[48,105] While high operating temperatures are common for different types of solar cells (and likely contributed by glass packaging), thermal instabilities of mixed cation perovskite solar cells, in particular wide band gap devices used in tandem,[64] require the development of better thermal management strategies to achieve long lifetimes. For example, a reduced degradation in performance for an Al sheet cover compared to cover glass has been reported for outdoor

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testing.[76] Thermal management is also particularly relevant for devices with carbon electrodes, since IR absorption by carbon would lead to significant heat trapping in the package if cover glass is used.[76] Thermal management is also expected to be important for conventional devices with metal electrodes, since the use of spiroOMeTAD and/or MoO_x as a part of the electrode makes this type of device more vulnerable to exposure to elevated temperatures.

In addition to thermal management, practical applications will also likely require the integration of effective encapsulation for long-term stability with the lead containment. While several possible solutions have been suggested recently, the number of publications dealing with this issue is still quite low. In general, the integration of lead containment features into an encapsulation package should be subjected not only to testing for lead leakage from damaged devices but also to standard stability tests to verify whether added features for lead containment can remain stable under damp heat conditions, or if they would exhibit a change in optical properties when exposed to prolonged solar illumination, etc. In addition, the use of additional cover glass to introduce a lead sequestration material between the substrate and the outer cover glass will likely result in worsening of the thermal management and consequently lower stability. On the other hand, lead adsorbers could be introduced as a coating on top of the passivation layer or as additives to the encapsulant (although this would require careful optimization of the mechanical properties), in addition to the thin film coating on the substrate (since the light is incident through the substrate and thus substrate glass is at risk from breakage due to hail impact).

Finally, both improvements in encapsulation and overall device stability would benefit from further accelerated testing which could be completed in significantly shorter periods of time compared to standard accelerated tests. This typically involves performing the testing under higher stress conditions compared to standard tests until desired improvement is achieved, followed by performing standard tests for the purpose of reporting the stability, since standard accelerated tests provide a verification of good lifetime.

7. CONCLUSIONS AND FUTURE OUTLOOK

PSCs have achieved significant progress not only in efficiency but also in stability compared to the early days of perovskite research. Consequently, despite the prevalence of shelf life stability testing, there is increased interest in stability testing following more stringent testing protocols introducing multiple stressors. Generally, for a reasonably reliable evaluation of device stability, it is advisable to include some form of testing with exposure to elevated temperature, exposure to humidity, and exposure to illumination, and thus, for example, a combination of damp heat test with either outdoor testing or MPP tracking under simulated solar illumination in ambient air would be a necessary minimum of tests needed to demonstrate that the devices have good stability. Combining high temperature tests with tests under illumination is important to demonstrate overall stability, since it has been shown that devices exhibiting excellent damp heat stability (>1800 h) can still show significant degradation during MPP tracking (with temperature increase to 45 °C for less than 1 day), which was attributed to the fact that devices containing TiO_2 have lower stability when exposed to UV illumination.[12] To achieve long device lifetimes under harsh testing conditions involving high humidity, it is necessary to effectively encapsulate the devices. A variety of encapsulation methods and materials have been reported to date, and some of those have resulted in demonstrations of stable performance of devices under damp heat and/or outdoor testing. Nevertheless, the reports of damp heat and/or outdoor testing remain scarce, and the use of encapsulations which are not suitable for such tests (simple epoxy encapsulation) remains common. Since the epoxies do not have suitable mechanical properties to ensure good adhesion when exposed to elevated temperatures or a wide range of temperature changes which would result in delamination, their use should be phased out (other than for stability investigations requiring disassembly of packaged devices where epoxy edge sealants are convenient, or for shipping samples to other laboratories for various measurements where disassembly of the package is needed to conduct the measurement).

Among different encapsulation methods and materials, PIB encapsulation in particular has been shown to be effective for damp heat tests and thermal cycling tests.[56] It has been used both in blanket encapsulation and as an edge sealant in combination with different encapsulants. Compared to damp heat tests, PIB has been less commonly used in outdoor testing, but it has been demonstrated to be adequate for outdoor testing. PIB tapes are readily available and are relatively straightforward to use and most likely would yield superior performance compared to various epoxies. The widespread use of PIB tape would enable easier comparisons of stability tests of encapsulated devices in different laboratories for works focusing on improving device stability rather than encapsulation, although further development of encapsulation is still needed to address the unique challenges of PSCs, due to the fact that perovskite layers or charge transport layers can be easily damaged by high temperature, solvents, or outgassing/decomposition products of the encapsulant.

While the simple use of PIB tape, especially if combined with an additional outer edge seal to protect the PIB, is likely adequate for achieving 1000 h of stable performance under damp heat and/or outdoor testing protocols, it is not sufficient to fully maximize the operational device lifetime. The ideal encapsulation would contain the following elements: (a) thin passivation layer, similar to that used in OLED encapsulation, preferably deposited by either solution processing or thermal evaporation to minimize the number of processing steps and transfer of devices from one deposition equipment to another; (b) encapsulant which does not damage the perovskite and exhibits good adhesion (possible choices: POE Enlight, TPU); (c) edge sealant, a desiccant filled PIB with outer edge sealant to protect the PIB; (d) nonpermeable cover (glass or metal for better thermal management); and (e) integrated lead sequestration. Further research is needed in the integration of the lead-sequestration function into the device package to demonstrate functionality under different standard accelerated stability testing protocols.

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Notes

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