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Encapsulation against Extrinsic Degradation Factors and Stability Testing of Perovskite Solar Cells

Edwin Ramírez, Rafael Betancur, Juan F. Montoya, Esteban Velilla, Daniel Ramírez and Franklin Jaramillo

Abstract

Commercialization of perovskite solar technology depends on reaching a stable functioning of the devices. In this regard, both intrinsic (chemistry phenomena of the different device layers) and extrinsic factors (environmental) need to be considered. In this chapter, we report the state of the art of encapsulation techniques against extrinsic degradation mechanisms. Our analysis includes the most common encapsulation structures, materials employed and their by-products, standard methods to test the stability of the devices (accelerated testing, outdoor and degradation monitoring), and security requirements to prevent the health/environmental hazard of lead leakage.

Keywords: encapsulant materials, extrinsic degradation, stability measurements, perovskite, solar cells

1. Introduction

Commercialization of perovskite photovoltaic technology (PPT) relies on the golden triangle of solar cell performance whose vertices are lifetime, cost, and efficiency. In the last years, PPT has achieved photovoltaic conversion efficiency (PCE) up to 25.7% at lab scale, almost matching their silicon counterparts [1]. Moreover, the impressive advances in the fabrication of solar modules by scalable solution deposition techniques [2] such as doctor blade, slot-die, or ink-jet printing have enabled a rapid performance growth of large-area devices. According to NREL, the PCE of perovskite modules has increased from 11.8% to 17.9% in the last 4 years. Also the scale of devices has evolved from “Submodule” with an active area of 200–800 cm², to “Small module” with area ranging from 800 to 6500 cm² [3]. A recent techno-economic model established a cost range for solution processed perovskite modules of \$3.30/W–0.53 USD/W [4], which is competitive with silicon solar cells. The low cost projected for PPT is linked to the processability by scalable solution-based deposition techniques. Therefore, the figures of merit for cost and efficiency of perovskite solar cells (PSCs) are almost pairing, in few years—those achieved for silicon after decades of technological development. However, the recent record for stability of PSC reached

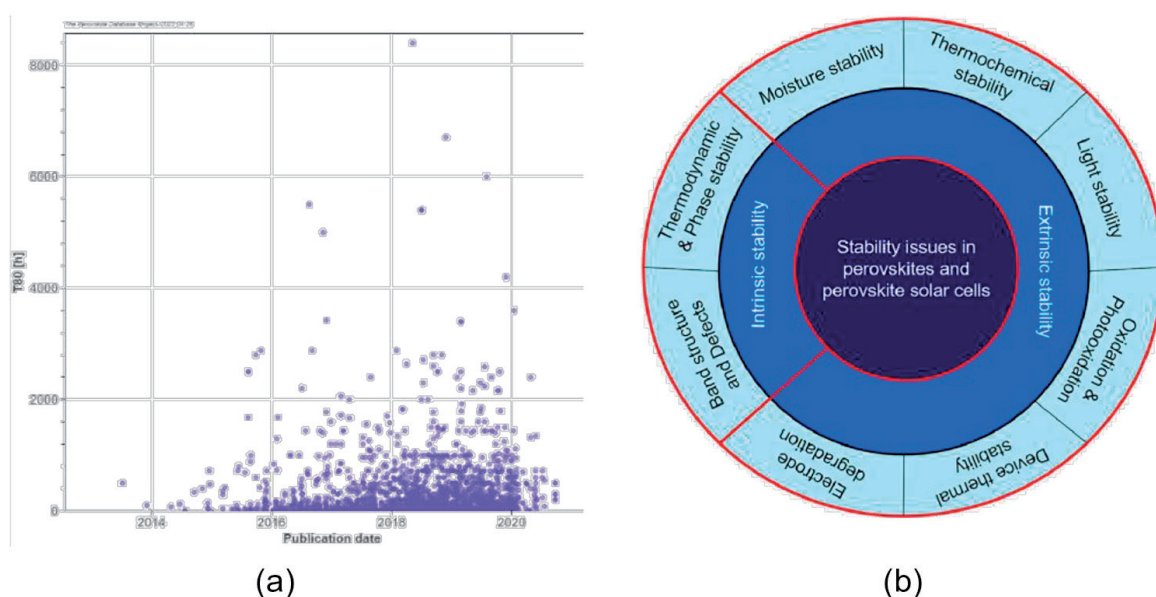


Figure 1.

(a) State of the art of the stability of perovskite photovoltaic (PV) devices based on the data available in the open-access Perovskite Database [6], and (b) stability issues in perovskite solar cells. Reproduced with permission from references [6, 7].

9000 hours under operational tracking [5], which is far behind the proven lifetime of 25 years (>200,000 hours) reported for silicon solar cells.

In recent years, several research articles have reported stability measurements of perovskite solar cells. **Figure 1a** shows the historical evolution of T_{80} for 1833 PSC devices recorded in the Perovskite Database [6]. T_{80} is a figure of merit defined as the time taken to observe a drop of 20% in the initial power output of the solar cell. Before 2016, only few articles reported T_{80} because the main focus was related to improving efficiency and processability of PSC. Since then, an increasing number of scientific articles report the T_{80} of PSC devices achieving in most cases values up to 1000 hours. Noteworthy, less articles report $1000 \text{ hours} < T_{80} < 2000 \text{ hours}$ and only a small proportion surpasses 2000 hours. This analysis of the scientific literature reveals the urgent necessity of increasing the PSC lifetime targeting to hundreds of thousands of hours.

A complex interaction of factors determines the stability of perovskite solar cells as shown in **Figure 1b**. Devices are degraded by multiple variables such as heat, light, electric load, moisture, and oxygen, which act simultaneously in real operation conditions. Such complexity explains why the progress in stability remains behind the rapid advancements in PCE and processability of PSC. Thus, understanding the degradation mechanisms is of crucial importance to overcome stability issues. Degradation mechanisms can be classified into *intrinsic*, which are related to the compositional and crystallographic structure of the perovskite material, and *extrinsic*, associated with the interaction of the PSC with external factors during their operational life.

2. Intrinsic and extrinsic degradation mechanisms

2.1 Intrinsic degradation mechanisms

Hybrid halide perovskites (HHPs) have been considered as “soft crystalline materials” due to their low formation energy and stability dictated by a delicate

thermodynamic balance [8]. Active layers of solar cells have been obtained from HHPs with the general chemical formula ABX_3 , where A is an organic or inorganic cation, B is a metallic cation, and X is a halogen anion. This structure has enabled the use of a wide range of atoms as A cations or X anions without significantly losing their high photovoltaic (PV) performance [9]. However, the structure can only accommodate a certain combination of ions due to restriction of sizes in order to have a stable cubic or tetragonal 3D structure. This restriction is often expressed by the Goldschmidt tolerance factor (t), which is calculated in terms of the ionic radii of the constituent ions. The 3D perovskite structure is favored by $0.8 < t < 1$ [8]. In halide perovskites used for PV, the A-site is a monovalent cation, commonly methylammonium ($CH_3NH_3^+/MA^+$), formamidinium ($CH(NH_2)_2^+/FA^+$), cesium (Cs^+), or a combination thereof. The B-site is a divalent metallic cation, mostly lead (Pb^{2+}) but in some cases can be tin (Sn^{2+}), and the X-site is a halide anion that is commonly iodide (I^-) or bromide (Br^-). A stable structure must preserve charge neutrality. Therefore, the valences of A and B should sum the charge of X multiplied by three. The mentioned restrictions in sizes and charges of the constituent ions determine that only certain perovskite formulations are stable at operational temperature ranges. For instance, the archetypical methylammonium lead iodide ($MAPbI_3$) has a tolerance factor of 0.911 forming a tetragonal structure at room temperature. This phase is stable up to 327.4 K turning into a cubic structure at higher temperatures [10]. During the fabrication of perovskite films, as well as during the solar cell operation, the material is subjected to temperature cycles that can promote the formation of unwanted PV inactive phases. This phenomenon has been observed for formamidinium lead iodide ($FAPbI_3$), which crystallizes into a non-perovskite hexagonal phase (yellowish phase) at room temperature due to its high tolerance factor ($t = 1.04$). This perovskite turns into a cubic structure after annealing over 150 °C [7]. $FAPbI_3$ -based PSC devices have been developed motivated by the higher thermal stability of FA^+ compared with MA^+ cation, but a careful material processing is required in order to avoid the formation of the non-active hexagonal phase of $FAPbI_3$. Although pure $FAPbI_3$ or $CsPbI_3$ perovskites yield higher thermal stability of the A-site cation, they are not the preferred choice due to thermodynamic phase stability issues. Alloys of A-site cations have been used to produce materials such as $FA_xCs_{1-x}PbI_3$ or $FA_{0.75}MA_{0.15}Cs_{0.1}Pb(I_{0.83}Br_{0.17})_3$ used as active layers in high performance devices [11]. Thus, compositional tuning is a suitable strategy to overcome thermodynamic stability issues. Note that the proportion between the A-site cations must be strictly controlled to achieve a suitable tolerance factor. In addition, since the perovskite bandgap depends in part on the energy level of the anion occupied p orbital, such compositional tuning also determines the resulting bandgap.

The benchmark $MAPbI_3$ perovskite has shown high defect tolerance preserving its opto-electronic properties even at high trap density (10^{14} – 10^{16} cm^{-3}). In contrast, PV grade gallium arsenide (GaAs) must have a defect concentration as low as 10^7 cm^{-3} [12]. This high tolerance to defects enables the synthesis of HHPs by solution processing techniques. Density functional calculations show that the growth conditions of the perovskite correlate with the concentration and type of defects. Specifically, the I/Pb ratio determines the formation energy of defects. It was found that formation energy of deep trap states is very high, therefore the probability of having nonradiative recombination centers is low. As a result, shallow trap states found in the $MAPbI_3$ perovskite are not detrimental of the photovoltaic performance [13]. This outstanding defect tolerance of the $MAPbI_3$ perovskite derives from its exceptional band structure. Notably, related perovskites with compositional mixtures at the A-site cations or

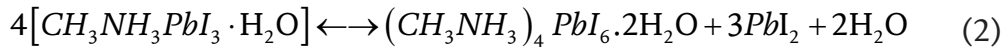
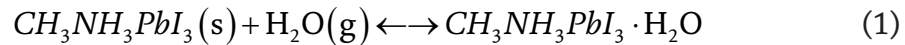
halides have also shown defect tolerance if they have an adequate Goldschmidt factor. Accordingly, a HHP with high structural stability is also defect tolerant.

In summary, compositional tuning is a suitable strategy to increase intrinsic stability, which means a thermodynamically stable structure with high defect tolerance. Both properties are of utmost importance for a photovoltaic material.

2.2 Extrinsic degradation mechanisms

Beyond compositional tuning, additional strategies must be developed to increase extrinsic stability. During solar cell operation, the perovskite active layer may interact with external factors such as heat, light, moisture, oxygen, electric bias, and other interface or external agents. Here, we briefly review some of the most important degradation mechanisms. Further information can be found elsewhere.

Water: When water interacts with perovskite, it can form hydrate or dehydrate phases according to reactions (1) and (2).



These reactions are reversible. Thus, perovskite can be regenerated exposing it to an inert environment. However, some irreversibility can appear due to phase segregation. Water forms hydrogen bonds with the A-site cation weakening its interaction with the lead halide octahedra [14]. As a result, the perovskite becomes prone to degradation by external other stressors such as heat or electric bias. Once the perovskite is saturated by moisture, it fully decomposes to PbI_2 and MAI.

Heat: During solar cell operation, the device is subjected to temperature cycles. As mentioned before, PV active phases of perovskites are stable in a temperature range. Moreover, some A-site cations are volatile organic molecules, which can be converted into gas-phase products when the perovskite reaches some critical temperatures. For instance, the MAPbI_3 can be decomposed to PbI_2 , ammonia and methyl iodide when it is heated to 85°C in an inert atmosphere [15]. Additionally, the materials commonly used in hole or electron transporting layers are organic molecules, which can also be degraded at some temperatures. The main strategies to avoid degradation by heat are compositional engineering of the A-site cation and encapsulation with materials with good heat dissipation properties.

Light: light-induced degradation has been attributed to the migration of vacancies in the perovskite layer [16]. UV degradation takes place in the absence of moisture and particularly in the device stack denoted as n-i-p, especially those containing TiO_2 , which can induce photo-degradation. However, it has been demonstrated that UV-degraded devices can be subsequently recovered by 1-sun light soaking. The UV degradation/recovery phenomenon has been attributed to the free carriers generated by light soaking after neutralization of accumulated trap states and generated free charges [17].

Moreover, light can induce redistribution of halide and metal ions in the MAPbI_3 perovskite film. This phenomenon causes the increment of the photoluminescence under illumination due to the diffusion of I^- species [18]. Ionic migration leads to phase segregation in the perovskite layer with halide-rich or halide-deficient areas being the most commonly found. These defects are carrier trapping states with

smaller bandgaps, which generate the increment in the photoluminescence. In the presence of moisture or oxygen, this phenomenon is more pronounced due to the passivation effect of superoxide molecules generated by the reaction of O_2 and H_2O with light [19]. In alloyed perovskites, light-induced A-site cation segregation has also been observed [20].

The main strategy against extrinsic degradation mechanisms is based on the encapsulation process, which is reviewed in the following.

3. Encapsulant structures

The encapsulation of solar cells has been highly guided by the industrial experience with commercial silicon solar cells. In general, the components for encapsulating a solar device [22] are presented in **Figure 2**. The general requirements that each encapsulation component needs to meet in order to protect the perovskite solar cells from external degradation factors are summarized in **Table 1**. These components include:

3.1 Polymeric encapsulant

It is the most critical component (also known as pottant or filling material). The list of its requirements includes: excellent adhesion properties, optical matching for better sunlight injection, electrical insulation, mechanical support, serves to physically separate cells and strings, UV stability, mechanical strength, thermal conduction, and stands thermal cycles. In addition, the selected encapsulant needs to adapt to specific processing conditions such as narrow temperature/pressure operational ranges and restrictions about the solvents and by-products that are considered “safe” to interact with the solar cell during the encapsulation process. Typical polymeric encapsulant materials are ethylene-vinyl acetate (EVA), PVB, TPU, silicone, ionomer, and UV-curable resin. However, it is important to mention that some devices, mostly at research level, do not include a polymeric encapsulant precisely to prevent device affectation after the interaction of the solar cell with the encapsulation material. In such cases, it is common to find in the filling space a desiccant material [22]. Finally, the standard encapsulation process for commercial PV devices, for instance, silicon ones, includes two layers of encapsulant fully surrounding the solar cell and its electrical contacts.

3.2 Substrate (bottom barrier)

It provides mechanical support and must provide a good thermal conductivity and a physical barrier against weathering. Typical materials include:

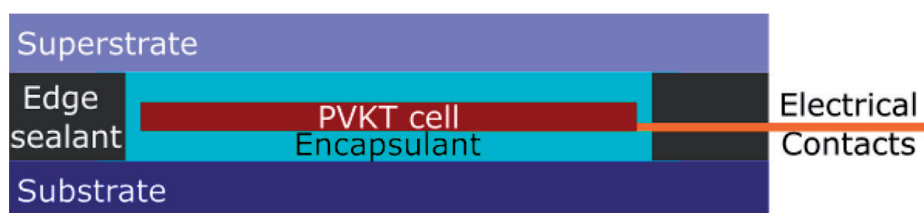


Figure 2.
Components used to encapsulate a perovskite solar cell.

General requirements		Encapsulation component			
		E	S	SP	ES
Mechanical	Resistance to break/tear		✓	✓	
	High adhesion strength between components	✓	✓	✓	✓
	Fixation of cells	✓			
Electrical	Insulation between cells/strings	✓	✓	✓	
	High dielectric breakdown	✓	✓	✓	✓
	High volumetric resistivity	✓	✓	✓	✓
Optical	High optical transmittance	✓		✓	
	Refractive index matching	✓		✓	
	Resistance to UV-induced yellowing	✓	✓	✓	✓
Physical protection	Low moisture absorption	✓	✓	✓	✓
	Low oxygen absorption		✓	✓	✓
Thermal	High thermal conductivity	✓	✓	✓	✓

E: Encapsulant; S: substrate; SP: superstrate; and ES: edge sealant.

Table 1.
General requirements of each encapsulation component.

- Glass
- Fluoropolymers-based: polyvinyl fluoride-based films such as Tedlar[®] and ethylene-tetrafluoroethylene-based films such as Tefzel[™].
- Tedlar-based: TPT (Tedlar/PET/Tedlar), TPE (Tedlar/PET/EVA), TAT (Tedlar/aluminum foil/EVA), TPAT (Tedlar/PET/aluminum foil/Tedlar), TPOT (Tedlar/PET/oxide/Tedlar).
- Polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) based: PAP (PEN/aluminum foil/PET), Teijin Teonex, BaSO₄-filled PET

3.3 Superstrate (top barrier)

It is the front barrier of the solar cell. Accordingly, it provides physical protection against weathering and serves as optical coupling for the injection of sunlight. Frequently, the superstrate includes surface coatings such as UV protection and antireflective coatings (ARC). Typical materials include:

- Glass: low-iron and tempered.
- Flexible glass.
- Flexible polymer ultra-barriers [23] Amcor, Viewbarrier (Mitsubishi Plastic Inc), Opteria, Tera barrier.

Typical names	Architecture
Complete encapsulation [23]. Blanket encapsulation with edge sealing [2].	
Blanket encapsulation [22]	
Edged covered encapsulation [24]. The structure is filled with inert gas.	
Film encapsulation [24]	
Russian doll encapsulation [24]. The structure is filled with an inert gas.	

Table 2.
 Encapsulation architectures.

3.4 Edge sealant

Its primary function is blocking the lateral ingress of oxygen and moisture. Typical materials are polybutyl (“hot butyl”), silicones, and polyisobutylene (PIB). An interesting integration between edge sealant with desiccant materials was achieved by Quanex (SolarGain[®]).

Clearly, different configurations of the encapsulation components enable several encapsulation architectures. **Table 2** shows the most common architectures. Be advised that there is not a universal labeling of these structures:

4. Encapsulation materials and by-products

The previous section mentioned the encapsulation structures that have been used for perovskite-type solar cells (PSCs). For the manufacture of these structures,

methods similar to those used for the encapsulation of silicon panels have been adopted, such as vacuum or roll-to-roll lamination processes [25]. These methods may include UV curing, high-pressure lamination, and temperatures between 80°C and 140°C to ensure good adhesion and avoid thermal degradation of the PSC [26]. The encapsulant materials must be chemically inert to the PSC layers and also serve as a barrier blocking extrinsic factors such as H₂O and O₂. In addition, the encapsulant materials must be stable under temperature, humidity, and illumination conditions, ensuring adequate electrical, optical, and mechanical properties of the resulting device (**Figure 3**). For instance, the materials used for FE (film encapsulant) and ES (edge sealant) must have a high volumetric resistance to offer electrical insulation, among these materials, EVA, Surlyn (ethylene methacrylic acid copolymer), and polyolefin (POE) have volume resistivities of 1×10^{14} , 6×10^{15} years 3×10^{16} Ω cm, respectively [27]. The main properties of the most studied materials used for FE and ES are presented below.

4.1 Optical properties

Mainly for FE, the materials used must present high optical transmittance since they are deposited on the active area of the solar cell and must guarantee that the light passes through. On the other hand, ES materials have fewer optical requirements since they are located in the non-active area of the cell.

EVA, Surlyn, polyvinyl butyral (PVB), UV-cured epoxy resins, polyurethane (PU), and POE have optical transmittance values around 90% [27]. However, the encapsulant EVA (the most common encapsulant used in commercial silicon cells) turns yellowish/brownish after a few years of operation leading to a decreased transmittance [28]. This is due to thermal stress of the copolymer, degradation by UV radiation, or a combination of both factors [28]. This outcome indicates that even for polymers that show high optical transmittance after the lamination process, it is necessary to perform accelerated aging testing under thermal and UV radiation conditions to confirm their durability. If after this kind of tests, the materials show a significant decay in transmittance, a possible solution is the incorporation of anti-oxidants, UV absorbing materials, or the use of Ce-doped glasses to absorb UV and prevent the aging of the encapsulant [29].

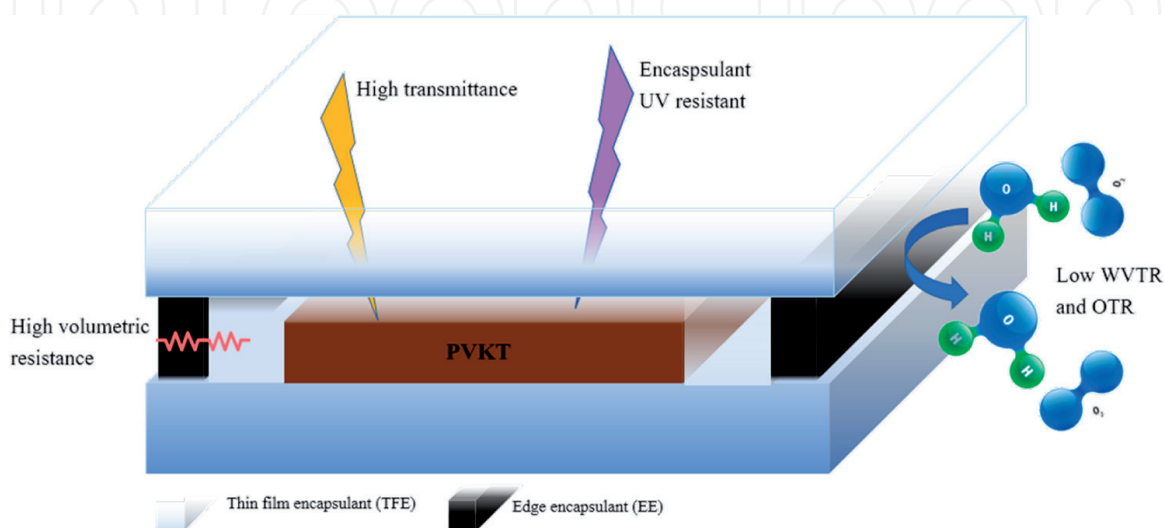


Figure 3. Scheme of complete encapsulation system.

4.2 Mechanical properties

The materials used in FE and ES must have a low elastic modulus in order to relieve strain and avoid delamination processes. The copolymers EVA and POE, mainly used in FE, have an elastic modulus between 10 and 80 MPa [27]. On the other hand, Surlyn copolymer has an elastic modulus around 400 MPa. For this reason, it has been reported that due to the brittleness of this material, delamination occurs after several measurement cycles [30]. These polymeric materials with low elastic modulus that minimize the presence of cracks under applied stresses are promising candidates for encapsulating flexible perovskite-based devices.

Among the materials that have shown the best results as edge sealing against moisture and oxygen are PIB and glass frits [25, 31]. PIB is a more versatile material with a low modulus of elasticity (9 MPa), which makes it a candidate for rigid and flexible encapsulation systems, while glass frits and epoxy resins are an option for encapsulation in rigid substrates, due to their mechanical rigidity making them prone to cracking. In addition, as further limitations, glass frits require temperatures $>100^{\circ}\text{C}$ for curing and currently are costly [25].

Solar cells must operate in ambient conditions, and it is necessary to anticipate the mechanical behavior of the encapsulating materials in different temperatures. For this reason, they are usually subjected to a thermal cycling test between -40°C and 85°C [27]. The glass transition temperature (T_g) of the encapsulant should be low enough to prevent the encapsulant from embrittlement in low-temperature conditions and failure, resulting in water and oxygen ingress and subsequent degradation. Polymeric materials that have a lower T_g usually have a lower cross-link density, a more flexible structure, and a higher free volume. For instance, the nonpolar chains in Surlyn are grouped together, and the polar ionic groups attract each other. This condition allows the polymer to behave similar to cross-linked polymers being more rigid and less permeable (**Figure 4a** and **b**), whereas EVA has a polymer structure that results in a more flexible but more permeable structure (**Figure 4c**).

4.3 OTR, WVTR, and prevention of volatilization of internal decomposition products

Due to the chemical nature of perovskite solar cells, the main purpose of the encapsulation is to mitigate degradation by extrinsic factors H_2O and O_2 . Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) are the parameters that allow to quantify the water vapor and oxygen that penetrate through an encapsulant film in specific conditions of temperature and relative humidity. Because water molecules are smaller than O_2 molecules, WVTR is used frequently to characterize the barrier properties of the encapsulant. It has been reported that the optimal

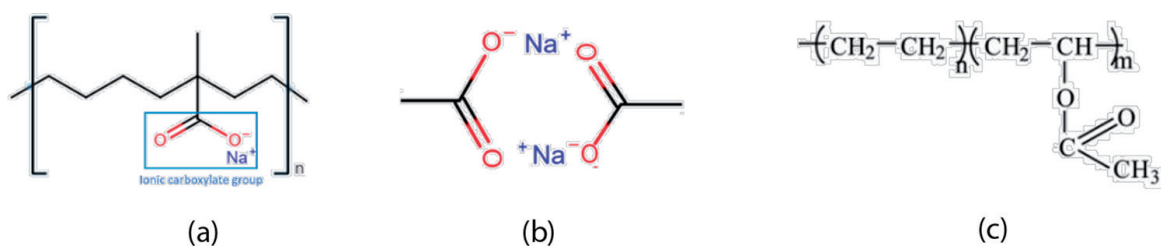


Figure 4. Polymer molecules: (a) Surlyn, (b) ionic interaction in the Surlyn copolymer, and (c) EVA.

encapsulation materials should have WVTR between 10^{-3} and 10^{-6} $\text{gm}^{-2} \text{day}^{-1}$ [24]. However, the WVTR varies greatly and depends on both the structure of the polymer and the polarity of the molecules. The nonpolar groups in the polymers are associated with low water affinity and result in surface contact angles >90 degrees. For instance, the thermoplastic polyurethane (TPU) has nonpolar groups and presents a contact angle around 150 degrees. This hydrophobicity allows the PSC modules encapsulated with this material retain 97.52% of the initial efficiency after 2136 hours under outdoor conditions [26].

In addition, to prevent extrinsic degradation, the materials used for FE can also contribute to reducing intrinsic degradation. Under stress factors, perovskite can decompose into volatile species such as HI, NH_3 , and CH_3I [25]. However, in the low confined volume of FE/PVSC, the partial pressure of the degradation of volatile species starts to be high, up to the equilibrium point where the decomposition reactions are suppressed. For this reason, the materials used as FE are of special interest, but the reactivity with perovskite layers and the possible formation of by-products must be studied [32].

4.4 Chemical properties and by-products

Materials used in FE must be chemically inert to PSC under UV-Vis radiation, ambient temperature, and high humidity conditions, while those materials used in ES must not release substances that degrade perovskite during thermal, UV, or laser curing. On the other hand, organic encapsulants should have resistance to UV degradation and should not present hydrolysis reactions, for instance, PDMS, POE, PIB, and glass frits have not exhibited any reactions that promote the degradation of perovskite or the material itself in accelerated aging tests. On the other hand, materials such as EVA and Surlyn under prolonged illumination and thermal stress produce acetic acid and acid methacrylate as by-products, respectively [22]. PU has ester bonding ($\text{R-NH-COOR}'$), which in the presence of high humidity leads to hydrolysis and depolymerization [33]. Similarly, it has been reported that PVB, due to its chemical structure, is sensitive to hydrolysis reactions and should be combined with low WVTR edge sealants [34]. On the other hand, the components of UV curable epoxy resins might be inert with PSC but have traces of moisture among them that subsequently degasify and degrade the perovskite layer.

Finally, most of these encapsulation materials are compatible with silicon cells, including EVA with acetic acid as a by-product. However, for PSC encapsulation materials with higher stability are required. Among these, PDMS, polyolefin, and PIB are shown to be the main candidates for encapsulation. Besides, to mitigate intrinsic and extrinsic degradation, the most promising structure is complete encapsulation, with an FE material that has high compatibility with PSC and an edge sealant with the lowest WVTR.

5. Stability testing and characterization

The main parameter to evaluate the stability performance of solar panels is the maximum power (or the panel efficiency), which depends on environmental variables such as solar irradiance and panel temperature [35]. In this context, the failure of an individual device is defined as the time at which the output power drops to 20% below the initial rated power. This parameter corresponds to the standard definition

of the lifetime of photovoltaic devices (T_{80}) used as a figure of merit and commonly estimated from regressions analysis using the maximum power as a function of time [36]. Moreover, T_{80} depends on different factors such as the materials and procedures used to fabricate the device, weather, and installation conditions, etc. [37]. Nevertheless, to improve the lifetime, the solar panel must include encapsulation/packaging materials to mitigate degradation processes, increase the electrical insulation, and provide mechanical and thermal support [38].

Delamination or adhesion loss of the encapsulant can be considered the most frequent and severe cause of module degradation, affecting the sunlight absorption and allowing the water-moisture penetration into the device [39]. In addition, most of the recognized failure modes on PV silicon modules are related to the packaging materials [40]. **Figure 5** shows the relationship between the device degradation and some failure modes such as discoloration, hydrolysis, corrosion, current leak, encapsulant embrittlement, and delamination. Herein, the degradation occurs when the substrate (backsheet) or encapsulant (typically EVA) is mainly affected by UV, heat, or water ingress. Besides, **Figure 5** correlates the involved tests according to the failure modes. For example, visual inspection and/or thermographic analysis (IF image) for discoloration, delamination or cell crack, chemical degradation for hydrolysis, series resistance (R_s) for the corrosion process, insulation test for leaking currents, and validating the status of the packaging material as a dielectric, etc. Finally, the overview also highlights the importance of the I-V curve and the extracted parameters from this curve to track the degradation processes, such as fill factor (FF), series resistance (R_s), shunt resistance (R_{sh}), etc. [41–43].

In this context, PV manufacturers widely recognized international standards such as IEC 61215 to identify potential failures in silicon photovoltaic modules [44]. This qualification testing is based on three stress factors: light (irradiance and UV), heat, and moisture. Herein, the initial stabilization (exposing the modules to simulated sunlight) and characterization (visual inspection, performance, insulation, and leakage currents) are essential to verify manufacture label values (datasheet). The final stabilization and wet leakage current test are performed to determine the module degradation and evaluate the pass criterium. It is worth noting that the output power determination is performed after a defined cooling time. Thus, eight randomly selected modules are tested into five groups as shown in **Figure 6**.

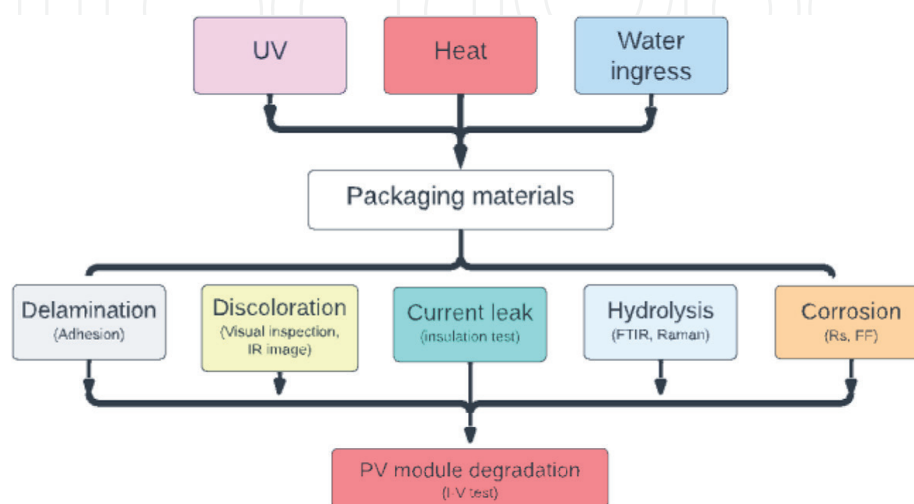


Figure 5. Correlation of failure modes with the packaging materials used in PV modules. Adapted from [40].

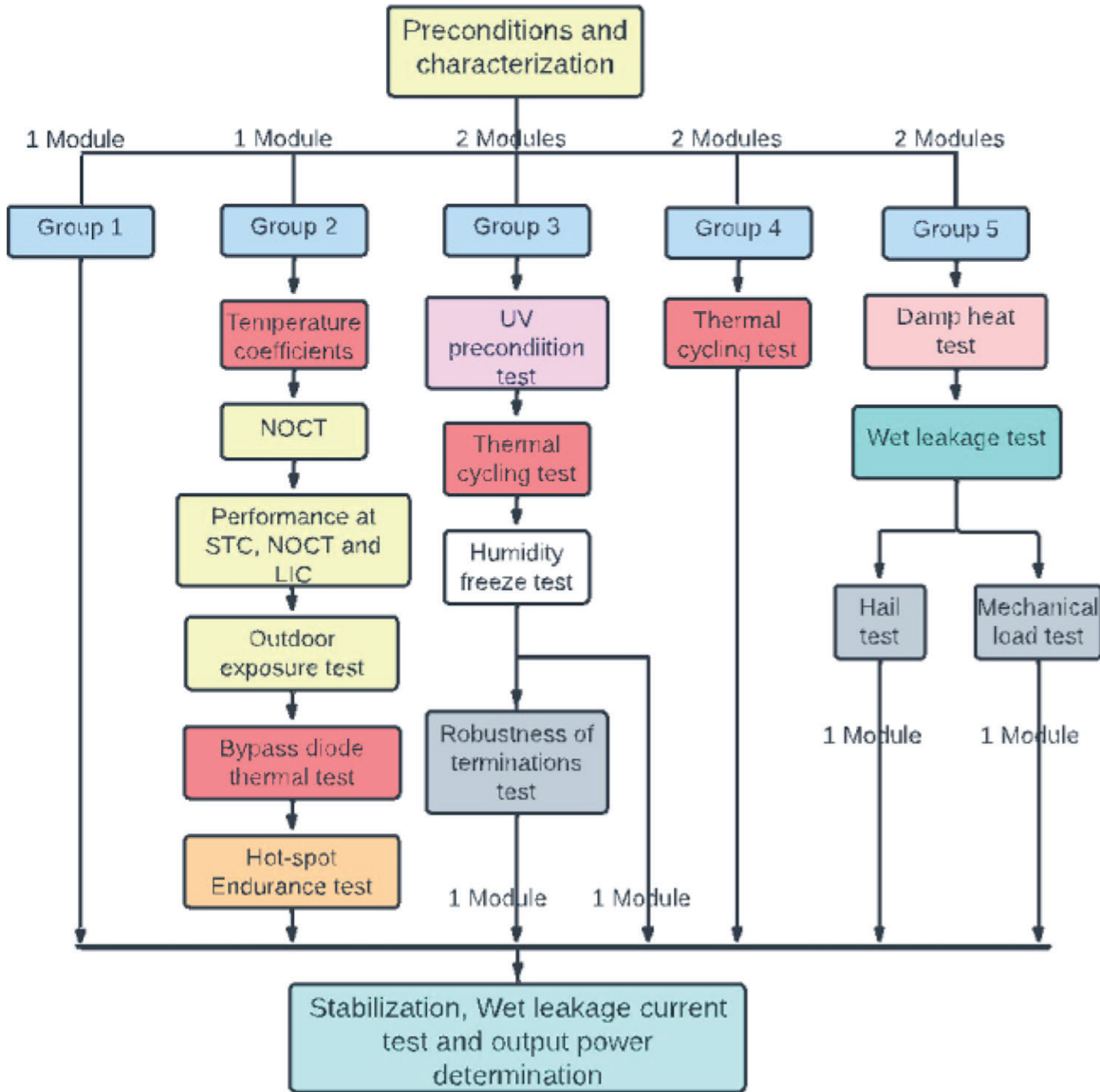


Figure 6. Flowchart for design qualification of PV modules according to IEC 61215. Adapted from [45].

- *Group 1:* one module is taken as reference (control).
- *Group 2:* one module is characterized considering the temperature coefficients and different power rating conditions such as standard test conditions (STC, irradiance of 1000 W/m^2 and module temperature of 25°C), nominal operative cell temperature conditions (NOCT, irradiance of 800 W/m^2 and ambient temperature of 20°C), and low irradiance conditions (LIC, irradiance of 200 W/m^2 and module temperature of 25°C). Moreover, the bypass diode and hot-spot are tested.
- *Group 3:* two modules are tested in order to determine the ability to withstand the temperature (thermal cycling) and humidity effects (humidity freeze test). In both tests, the applied current and experiment setup must follow the standard suggestions.
- *Group 4:* two modules are tested in order to determine the ability to withstand temperature changes (cycling test).

- *Group 5*: two modules are tested in order to determine the ability to withstand the humidity penetration (damp heat test, 85°C/85%RH). Moreover, mechanical tests are included.

In the case of perovskite solar cells and modules, a broad range of efficiencies have been reported due to the diversity of structures used in the fabrication, highlighting the critical role of the protocols for obtaining reproducible devices [2]. Moreover, several protocols have been designed to evaluate the stability of perovskite devices focused in laboratory-scale cells. From these, the protocol most widely spread is the result from the International Summit on Organic Photovoltaic Stability (ISOS) [46].

Related to the deployment of perovskite technology, several features must be highlighted from the stability tests reported in the literature. Ethylene-vinyl acetate (EVA) as an encapsulant has been successfully tested following the temperature cycles test suggested by IEC 61215 [30]. Polyisobutylene as a barrier layer showed promising results in thermal cycles and damp heat tests [47]. Carbon layer as a barrier increased the long stability of devices up to 12,000 hours of exposure under continuous illumination [48]. A printable mesoscopic solar cell with carbon as the electrode and hot melt polyurethane as encapsulant passed the accelerated tests suggested by IEC 61215 [5]. Epoxy resin was used as encapsulant to evaluate the outdoor performance for minimodules following the international standard IEC 61853-1 [49]. The lifetime of minimodules encapsulated with EVA was estimated in outdoor tests concerning the depicted degradations patterns for the maximum power evolution and ideality factor providing insight concerning the degradation processes [43].

Although a lot of work has been reported on the stability of perovskite technology, the average lifetime (T_{80}) is still short and reaches just a few months [50]. This fact remarks the essential role of the packaging materials to protect the solar cells and electrodes from the environment guaranteeing lower degradation rates. In fact, the stability results suggest that there is still room for improvement, particularly outdoor test investigations to provide insights related to failure modes [51]. Nevertheless, it is worth noting that the qualification testing does not test for all failure mechanisms, and for that, it cannot be used to provide a prediction of the device lifetime [52]. Besides, the qualification testing of IEC 61215 is proper for modules (module level); thus, the scaling of the technology and some particularities of the perovskite technology must be considered to adapt or include other requirements for testing the device stability, as occurred with the light-soaking effects (power stabilization) for thin-film modules [44].

6. Security

In addition to the relevance of encapsulation as an important aspect to overcome the extrinsic degradation and improve the operational stability of the PSCs, health and environmental security are also pertinent toward commercialization of the technology. Like other photovoltaic modules, such as silicon, Perovskite modules can be damaged due to several uncontrollable causes that could include hailstones, fire during operation, or some other natural disaster. Therefore, a proper encapsulation can also contribute to prevent environmental issues associated with constituent materials leakage. Particularly, lead represents the most hazardous environmental contaminant among all the constituent materials in a PSC. It has been estimated that for a typical 400–550 nm thick perovskite layer, the unit area concentration of Pb ranges from 0.4

to 0.75 g/m^2 [53, 54], which is a high value, when compared with the amount of lead present in an automobile battery that contains 20 pounds (9,000,000 mg) on average.

If a PSC made from a $\text{CH}_3\text{NH}_3\text{PbI}_3$ is in direct contact with water, it immediately decomposes into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ [55]. When a broken device is exposed to simulated rain, it loses up to 72% of lead after 5 min of leaching and 100% after 72 hours. In order to prevent contamination by lead leakage, there are basically two alternatives. The first one is to make a long-lasting encapsulation that can be “indestructible,” which is quite difficult to achieve, but somehow possible using a self-healing coating that could heal itself after any kind of scratch. The second strategy is focused on mitigating the leakage after the encapsulation has failed, by means of chemical lead sequestration, using lead adsorbents in the device structure. A schematic representation of these two strategies is shown in **Figure 7**.

In the case of lead leakage prevention using chemical absorbing materials, resins are the preferred choice. Among them, *P,P'*-di(2-ethylhexyl)methanediphosphonic acid (DMDP) and *N,N,N',N'*-ethylenediaminetetrakis(methylenephosphonic acid) (EDTMP) as Pb-chelating agents, or sulfonic acid cation exchange resins, such as Amberlyst15TMH, can be used [56, 57]. **Figure 8** shows two examples of these materials, one chelating resin and one cation exchange resin. In the first case, the two phosphonic acid groups in each DMDP molecule can strongly bind with a Pb^{2+} with a binding energy of 252 kJ mol^{-1} . In the second case, the sulfonic acid groups act as adsorption sites for Pb^{2+} ions and have a surface area ($\sim 50 \text{ m}^2 \text{ g}^{-1}$) due to its nanoscopically porous structure with nanoparticle sizes of $\sim 40 \text{ nm}$. As the two materials act when lead is in its ionic state, they can be introduced as an external coating of the device, but also in combination with the solid state perovskite film, in some cases without decreasing the device performance [56].

The use of a self-healing coating to prevent lead leakage is shown in **Figure 9**. Resins with low glass transition temperature (T_g) are attractive for this purpose. Specifically, epoxy resins with T_g below 50°C can be sandwiched between the

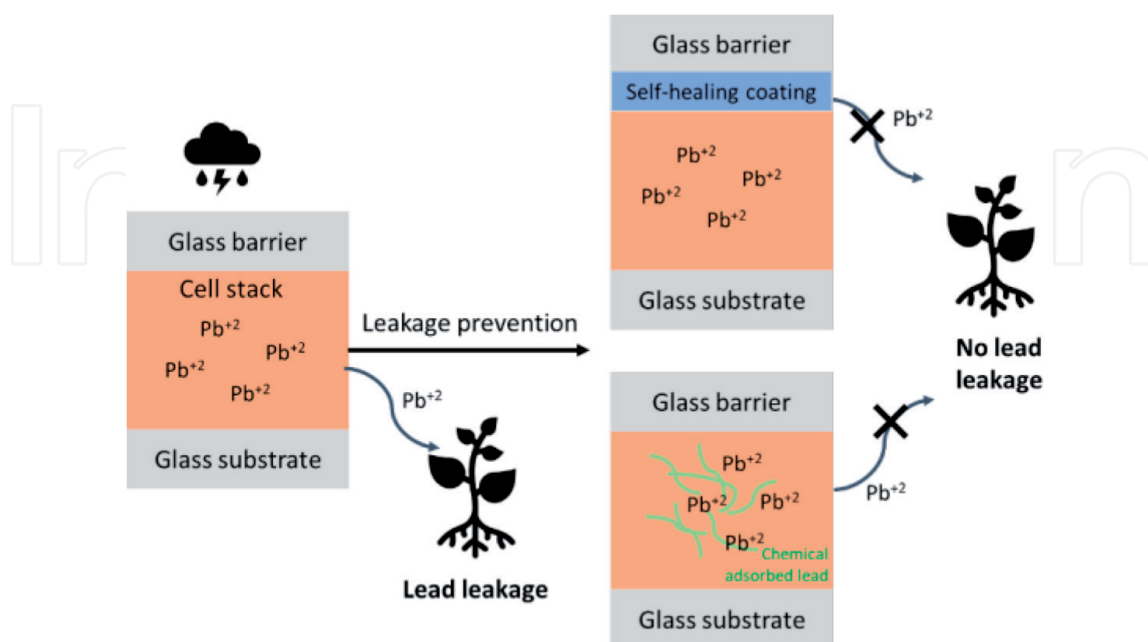


Figure 7.

If a solar cell is broken, the use of two strategies can prevent the lead leakage. The first one (top-right) is the use of a self-healing coating that can automatically repair if it is damaged, and the second one (bottom-right) is the use of an adsorbent chemical that can capture leached lead before it reaches the soil.

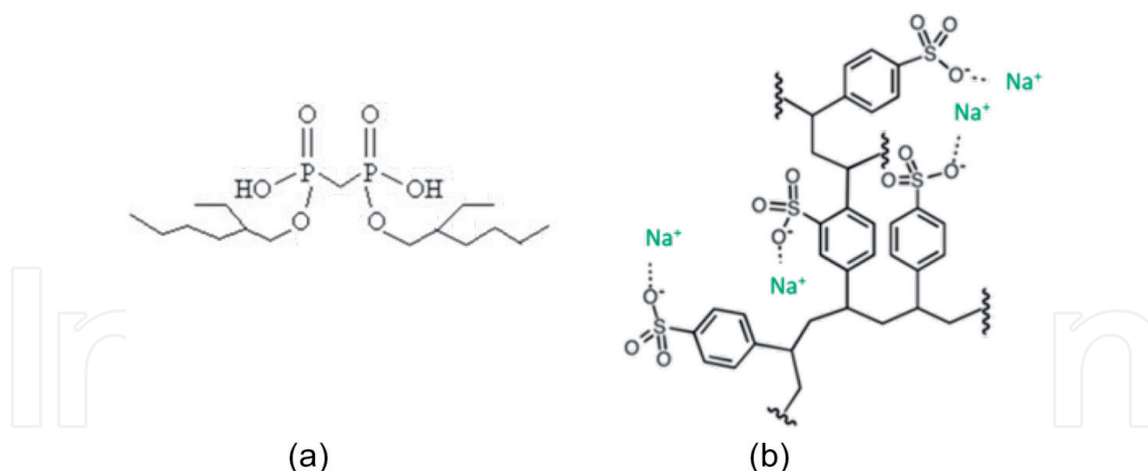


Figure 8.
Chemical structure of (a) DMDP resin, and (b) Amberlyst15TMH cation exchange resin.

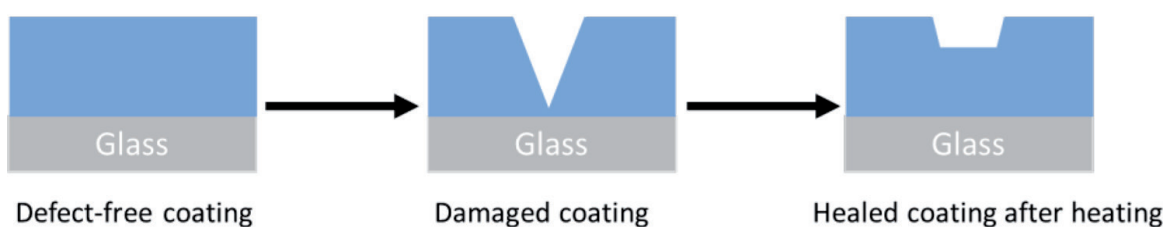


Figure 9.
Schematic representation of the self-healing process of a glass (gray) coated substrate that can be damaged and then recover after heating at low temperature (below 50°C).

perovskite solar module and the top glass cover, and when the glass and the coating are damaged, the heat caused by sunshine can increase the device temperature above T_g , leading to a softening of the epoxy resin and a structural accommodation that can fill the empty spaces (cracks or cut areas).

7. Conclusions

In line with the impressive advances in efficiency (25.7% at laboratory scale) and cost reduction associated with the fabrication of perovskite solar modules using scalable solution deposition techniques, the protection of perovskite solar cells against extrinsic degradation factors, such as moisture, oxygen, heat, and sunlight, is a matter of intense research toward reaching the golden triangle of solar cell performance (lifetime, cost, and efficiency). As reviewed in this chapter, the particularities to improve the lifetime of the perovskite technology have demanded three main aspects:

Innovation in encapsulation materials fully compatible with the perovskite device structure from the chemical and processing frameworks. Up to date, PDMS, polyolefin, and PIB are the main candidates as encapsulants, and the complete encapsulation with edge sealing is the most promising structure to prevent H₂O and O₂ ingress and decrease degradation into volatile components.

Adapting the testing methods to better characterize and predict the temporal performance evolution of the perovskite devices and their failure mechanisms.

Finding alternatives to mitigate the environmental hazard of lead leakage where self-healing encapsulation structures and lead sequestrants outstand.

By consolidating all of these aspects have the potential to reach a robust encapsulation solution that paves the way for commercial perovskite solar cells.

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