Quantifying Performance of Permeation Barrier—Encapsulation Systems for Flexible and Glass-Based Electronics and Their Application to Perovskite Solar Cells

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Effective transparent barrier/encapsulation systems represent a key enabling technology for large-area electronics. Securing stability to the environment is vital. Here, the effects of architectures, application processes, and water vapor transmission rates (WVTR) of transparent flexible ultra-high permeation barrier films (UHPBF) applied to substrates with adhesive resins are unraveled for attaining long lifetime, and compared with polyethylene terephthalate and glass barriers. How strongly performance of barrier/adhesive systems depends on barrier orientation, adhesion, manipulation, defects, and storage procedures is quantified via calcium tests. Furthermore, it is found that introducing an additional adhesion-promoting layer on the standard UHPBF stack reduces WVTRs by a factor of 5 compared to barriers without it. Finally, barriers are used for sealing and encapsulation of perovskite solar cells (PSCs) enabling the extraction of a relationship between WVTRs of barrier/adhesive systems and degradation rates (DR) of PSCs. DR fall exponentially when WVTRs decrease from $10^1$ to $10^{-3}$ g m$^{-2}$ d$^{-1}$. Outside that range any gains or losses are mitigated by tailing of the sigmoid curve relating the two parameters. Results highlight important factors which will help those developing strategies relating to encapsulation, barrier, adhesive and sealant systems and stable optoelectronic devices on glass and flexible substrates.

1. Introduction

The industry of large area optoelectronics is progressing rapidly. From solar voltaic modules to flat panel displays, the

markets for the more mature technologies, and research for the emerging technologies, are increasing year by year. Among these are organic, metal oxide, and organo-hybrid perovskite semiconductor transistor, light-emitting diode, and solar cell-based systems.[1–4] Large-area optoelectronics is developed on rigid (mainly on glass) and flexible (mainly on plastic such as polyethylene terephthalate, PET) substrates[5] with other types of substrates also being investigated such as paper,[6–7] flexible glass,[8] or textiles.[9] Organic light-emitting diodes (OLEDs), for example, are today one of the most commercialized technologies especially in small-display markets (e.g., smartphone displays) where they now take a major share of the market. In research laboratories, perovskite solar cells (PSC) have seen a huge interest reaching certified record efficiencies of 25.2% at standard test conditions (Air mass AM1.5G, 1000 W m$^{-2}$, 25 °C)[10] within only 10 years of development. Further they reach the highest power output densities under artificial indoor illumination (i.e., 20.2 µW cm$^{-2}$ at 200 lx[11]) which make them not only a bright candidate for energy harvesting outdoors but also for indoor IoT devices, sensors, and small consumer electronics[12] even for flexible substrates under artificial lighting.[13,14] The success of large area electronics in general lies in the advantageous properties of the materials used and in the fabrication processes (e.g., evaporation, sputtering or solution processing via printing techniques). These are also often compatible with flexible substrates.[15,16] Nevertheless, lifetimes of many of the constituent materials suffer when coming in contact with ambient moisture and oxygen[17–19] which can induce chemical degradation to the semiconducting, transport, and electrode layers.[20–22]

To avoid moisture and oxygen ingress and further degradation, devices must be encapsulated with permeation barriers ensuring a water vapor transmission rate (WVTR) range of $10^{-3}$ to $10^{-6}$ g m$^{-2}$ d$^{-1}$[23–28] and an oxygen transmission rate (OTR) between $10^{-2}$ and $10^{-3}$ cm$^3$ m$^{-2}$ d$^{-1}$.[29–32] Encapsulation
of rigid devices is relatively straightforward, where glass or metal sheets are applied with appropriate sealants. For flexible devices, especially where transparency of the barrier is required (e.g., for displays or photovoltaic modules), the solutions are more complex since plastics are highly permeable to gases. Currently, the encapsulation methods consisted in direct deposition of a protective thin films (i.e., Al₂O₃ or Parylene C[33–38]), or the application of permeation barrier film using a sealant or adhesive (e.g., epoxy, ultraviolet UV-curable or silicone-based resins, hotmelts, thermoplastic films, pressure sensitive or bifacial adhesives)[26,27] on the devices. Protective film deposition directly on the device typically, although effective,[38–41] requires the laboratory or industry to possess a high-cost vacuum-based equipment/process (e.g., atomic layer deposition—ALD) as well as detailed understanding of the interaction between the deposition process, the barrier layer material, and the device structure. The application of permeation barrier after production (by a lamination step) is more straightforward and applicable to all types of devices with a wide range of adhesive/barrier combinations available to the device engineer. Permeation barriers prevent the ingress of gas (i.e., water vapor or oxygen) due to inherent properties of the material or materials stacks such as hydrophobicity, low absorption or diffusion coefficient.[28,42–44] Glass has the best water/oxygen blocking properties as transparent material (WVTR < 1 x 10⁻⁶ g m⁻² d⁻¹[45]) and is a very affordable; however, it is mostly incompatible with flexible electronics: a market that has dramatically risen in the last years.[46] As an alternative, flexible ultra-thin glass was developed and used to encapsulate OLEDs, showing good permeation and flexibility properties but was susceptible to the cutting process which can lead to edge damage.[45] Flexible permeation barriers must meet the minimum WVTR and OTR requirements, and be compatible with the degradation of encapsulated optoelectronic devices, specifically for perovskite solar cells, which we evaluated under similar test conditions to those of the barriers. Currently, there are studies that correlated the barrier performance and the lifetime of organic solar cells (OSC). By studying the water diffusion through the barriers, Cros et al.[53] calculated that 3.5 g m⁻² are needed to degrade the power conversion efficiency (PCE) of an OSC by 50% when it is tested at 22 °C and 100% relative humidity (RH). Similarly, Hermenau et al.[54] showed that the quantity of water increase to 15.5 g m⁻² when OSC were tested at 45 °C and 5.5% RH. De Rossi et al.[56] first carried out a systematic investigation of flexible barriers on dye sensitized solar cells estimating that gas ingress by lateral permeation was the main culprit for permeation on small- and medium-sized cells. Notably, there are no reports unravelling the direct correlation between the permeation rates (i.e. WVTR values) and lifetime performance (i.e., PCE degradation) of encapsulated perovskite solar cells.

Here we measured the WVTR of different barriers: glass (for rigid devices), and PET film and a transparent flexible ultra-high multilayer permeation barriers (UHPBF) with different architectures and orientations for flexible devices applied to the substrate with a resin. With calcium tests we highlighted the effect of correct orientation, manipulation, and storage of different types of barriers. Also, we encapsulated PSCs with different permeation barriers and tested degradation rates under an ISOS (International Summit on Organic Photovoltaics Stability)-D-1 shelf life test.[57] PSC degradation rates (DRs) allowed us to extract the influence of permeation barriers and their WVTR on the degradation rates/failure of solar cells, and, for the first time for PSCs, an empirical relationship between the degradation rate of the cell and the WVTR of the applied permeation barrier/adhesive system.

2. Results and Discussion

First, we evaluated, with both electrical (i.e., monitoring the resistance of encapsulated calcium (Ca) sensors over time) and optical (i.e., monitoring the color of the calcium sensors over time) calcium tests (see Figure 1a), the performance of different barrier/adhesive systems. The UHPBF (see Figure 1b–d) were compared against plain PET films- and glass-barriers. Two different architectures of UHPBF were evaluated: PET/ZTO(zinc-tin-oxide Zn₂SnO₄)/ORMOCER(organic-inorganic hybrid polymer)/ZTO labeled as “UHPBF-R” (see Figure 1c), and one with an additional SiO₂CH₂ layer, that is, polyethylene naphthalate (PET)/ZTO/ORMOCER/ZTO/ORMOCER/ZTO/SiO₂CH₂ labeled as “UHPBF-S” (see Figure 1d). Subsequently we applied the barrier systems to perovskite solar cells carrying out ISOS-D-1 shelf-life tests to extract a relationship between WVTR of the barriers and degradation rates of PSCs.

The UHPBFs have proven to be a suitable option for the encapsulation of optoelectronic devices because of their low WVTR values. Generally, the UHPBFs are commercialized indicating “extrinsic" WVTRs which include all defects on a certain large-area (i.e., 70 cm²) as measured with the Wasserdampf-Durchlässigkeits (WDDG) water vapour permeability coulometric testers or on small-area (i.e., 3 mm diameter) with, for example, the Ca-Test.[54] According to the international standards such as to ISO 15106-3:2003 standard[56] and BS3177[59] the extrinsic WVTR is measured after the barrier fabrication at 38 °C and 90% RH. The extrinsic WVTR of the barriers and the respective technique used for its calculation are listed in Table 1 together with those experimentally determined for the barrier/ adhesive systems under investigation with our electrical Ca
tests, i.e. WVTR$_E$. To determine an interdependence between the encapsulation barriers and the lifetime of PSC, both barriers and solar cells must be evaluated under same test conditions. Thus, barriers were here tested at room temperature and relative humidity ($T=25^\circ C$ and $RH=35\%$) which are the parameters defined by the ISOS-D-1 protocol.

2.1. Ultra-High Permeation Barrier Films, Plastic Films, Glass Barriers versus No Encapsulation

The encapsulation barriers, including PET, glass, and the different UHPBFs, were tested under laboratory environmental conditions ($T=25^\circ C$ and $RH=35\%$). The electrical calcium test allowed us to extract the experimental water vapor transmission rates (labelled WVTR$_E$) which are reported in Table 1. The WVTR$_E$ represents the rate at which water passes through the barrier/adhesive system (at least until the Ca-sensor fails). The tests were conducted for no less than 1000 h. The experimental WVTR$_E$ values reported in Table 1 were calculated over an average of the five Ca sensors shown in Figure 1a. WVTR$_E$ represents an average that includes side permeation and top permeation with the error values expressing variations over all the encapsulated Ca sensors. To delve into the exact quantification of lateral versus top permeation would require a dedicated investigation but the sensors with the long edge closest to the substrate (i.e., sensors 1 and 5) on average led to degradation rates which were 10–70% larger than those of the more central ones (i.e., sensors 2–4). Data in Figure 2 represent average conductance values over 1464 h for the UHPBF-S and UHPBF-R barrier films compared to those with glass, a simple PET plastic film and no barrier applied. The UHPBF-S reduced average water vapor permeation by five and three orders of magnitude compared with samples without encapsulation or encapsulated with PET-only respectively (see Table 1). Samples encapsulated with UHPBF-S, for which WVTR$_E = (8.2 \pm 0.3) \times 10^{-4}$, retained 64% of their initial conductance which was 17.9% lower than samples encapsulated with glass (retaining 78% of their initial conductance with a WVTR$_E = (1.9 \pm 0.5) \times 10^{-4}$) in relative terms, possessing however additional characteristics of being flexible and light-weight, and compatible with R2R lamination processes. Finally, the inset photograph in Figure 3 shows five Ca-sensors encapsulated with UHPBF-S after 1464 h showing no macroscopic signs of degradation.

2.2. Ultra-High Permeation Barrier Films: Architectures and Their Application

When UHPBF-R was initially applied in the testing architecture of Figure 1a, it was applied over the calcium sample by hand (UHPBF-R (Air) No press) which led to an irregular coverage...
Table 1. WVTR of the different barrier/sealant systems. The extrinsic WVTR indicates the water permeation according to the test conducted by the barrier manufacturer following international standards, and the “Technique” column describes the method used for determining it. The WVTR ca was that experimentally determined with our electrical Ca test (see Figure 1) utilizing the method described in Section 4 (except for samples without barrier which were tested with an optical Ca-test due to very rapid degradation of the calcium). The aging tests were carried out at room temperature and relative humidity (T = 25 °C and RH = 35%) for more than 1000 h. All barriers were sealed to the calcium sensor substrates using E131 resin.

| Barrier | Adhesion | Extrinsic WVTR | WVTR ca [g m⁻² d⁻¹] (25 °C/35%) | Composition/Description |
|---------|----------|----------------|----------------------------------|------------------------|
| No barrier, no resin | – | – | 75 ± 25 | Sample without any encapsulation. Rather than being a conventional WVTR, it is a result of degradation of Ca in air. |
| Resin only | – | – | 11.6 ± 2.1 | Resin (E131) deposited on Ca sensor without barrier utilizing the PTFE slab to apply pressure uniformly. Thickness of the cured resin was measured to be 45 ± 6 µm. |
| PET | High | 2.9⁺⁻ | (4.4 ± 0.2) × 10⁻³ | Heat Stabilized PET, thickness = 175 µm dried and laminated (i.e using PTFE slab) in N₂ according to the procedure described in Section 4. |
| UHPBF-R | Low | <1 × 10⁻⁶ | (5.7 ± 1.2) × 10⁻³ | Structure: PET/ZTO/ORMOCER/ZTO Ultra-high permeation barrier film stored, dried and laminated with PTFE slab in N₂ according to the procedure described in Section 4. |
| UHPBF-R (Back) | High | (1.7 ± 0.3) × 10⁻² | UHPBF-R which was glued to samples on the back side (PET carrier substrate facing the sample). |
| UHPBF-R (Air) | Low | (3.2 ± 1.6) × 10⁻² | UHPBF-R which was stored in air and was not properly dried before its application in N₂. |
| UHPBF-R (Air) No press | Low | >5.4 × 10⁻¹ | UHPBF-R which was stored in air, not properly dried before its application in N₂, and resin did not cover the full area. |
| UHPBF-S | High | 4.0 × 10⁻³ | (8.2 ± 0.3) × 10⁻⁴ | Structure: PEN/ZTO/ORMOCER/ZTO/ ORMOCER/ZTO/ SiOₓCᵧHz The SiOₓCᵧHz layer improved the resin/barrier adhesion UHPBF-S was both dried and laminated in N₂ (i.e using PTFE slab) according to the procedure described in Section 4. |
| UHPBF-S D1 | High | (3.8 ± 0.1) × 10⁻³ | UHPBF-S but with defects produced by inappropriate handling. D1 represented visible pin-holes. |
| UHPBF-S D2 | High | (3.9 ± 0.2) × 10⁻³ | UHPBF-S but with defects produced by inappropriate handling. D2 represented cracks. |
| Glass | High | 1 × 10⁻⁶ | (1.9 ± 0.5) × 10⁻⁴ | Thickness of 1 mm Glued in N₂ according to the procedure described in Section 4. |

¹Calculated using the optical calcium test; ²Thickness of the other cured SY-QS bicomponent resin was (101 ± 20) µm and the WVTR ca of this adhesive only, applied with the PTFE slab, was (2.7 ± 1.3) g m⁻² d⁻¹; ³WVTR from material datasheet.

of resin and/or the presence of gas bubbles trapped between the barrier and calcium sensors. Consequently, the conductance degraded rapidly, failing at the 3 h mark (pink star in Figure 2). Compared to the extrinsic WVTR = 2.7 × 10⁻⁴ g m⁻² d⁻¹, calculated via Hergert optical calcium test which requires only perimetric application of glue and in which the calcium sensor is deposited directly on the barrier, the fast degradation of the Ca can be attributed to two main factors: an inefficient application of sealant, and/or the storage of barrier in air. We thus improved the application of the adhesive resin using a polytetrafluoroethylene (PTFE) rectangular slab to apply pressure uniformly over the whole barrier waiting for the sealant to set producing a homogenous resin film of thickness equal to 45 ± 6 µm. This procedure notably improved the operation time.
of the barrier from 3 to 60 h before complete failure (UHPBF-R (Air), cyan open triangle), but the performance was still lower than expected. This was the result of storage of UHPBF-R in air where it absorbs moisture. Barriers must be kept in an inert atmosphere (i.e., nitrogen (N₂) or Argon) and/or dried prior to their application. In fact, the barriers dried beforehand (UHPBF-R, dark green open square), as described in Section 4, showed an order of magnitude better WVTR ($4.5 \times 10^{-3}$ g m⁻² d⁻¹) than those that were not (UHPBF-R (Air)), indicating that any moisture present in the barrier can seep out into the device during time if not degassed properly. It is also important to apply the barrier in the right way: the side with oxide/ORMOCER multilayer stack must face the device. In fact, when one instead applies the PET side over the devices, the water permeation (Figure 2, orange open circle) increased by an average factor of 5.8 compared to applying the glue on the opposite side (Figure 2, dark green open square). This can be attributed to the high thickness and permeation of PET films (75 µm) which allowed side ingress of water through the PET and then into the devices. It must be noted that UHPBF-R presented us with some delamination and sealing issues upon application, likely indicating poor adhesion of the glue/resin with the final ZTO layer of the multilayer stack. We thus tested the UHPBF-S barrier which had an additional 50 nm layer of SiO₂C₁₂H₁₇ over the ZTO. By manipulation, it was clear that the adhesion of the UHPBF-S samples to the calcium sensors was significantly better than that of UHPBF-R. It was not possible to quantify the adhesion strength with our current set-up; therefore, the correlation between adhesion strength and WVTRs for encapsulation systems can be the focus of useful future studies. Even though the new UHPBF with SiO₂C₁₂H₁₇ (UHPBF-S) presented a similar extrinsic WVTR ($4 \times 10^{-3}$ g m⁻² d⁻¹) to that of prior UHPBF-R ($<1 \times 10^{-3}$ g m⁻² d⁻¹) using the test which requires only perimeter sealing (Coulometry test), the UHPBF-S performed considerably better (average WVTR of $8.2 \times 10^{-4}$ g m⁻² d⁻¹) than UHPBF-R being one order of magnitude less when tested glued to the device (Figure 2, blue square), as a result of a much improved adhesion which possibly led to a reduction of the interface diffusion.

### 2.3. An Analysis of the Effect of Defects in Ultra-High Permeation Barrier Films

In this section, we describe types of defects that can appear in barrier films that are not handled with appropriate care and their effect on UHPBFs. The defects we identified, mainly with our optical calcium test, were of two main types: pinholes (defect type 1, D1) and cracks (defect type 2, D2). These were produced by an inappropriate manual handling of barriers during cutting or lamination over the devices, or manufacturing defects. The WVTR of barriers that had cracks (labelled...
as UHPBF-D2), from which water ingressed rapidly, was only $3.7 \times 10^{-3}$ g m$^{-2}$ d$^{-1}$, one order of magnitude worse compared to barriers that had been handled properly and devoid of cracks (see Figures 3 and Table 1). Generation of defects of type 2 was eliminated when barriers were cut to size with a laser beam instead of a scalpel and handled with flat blunt plastic tweezers. Pinholes or D1 defects were, instead, more difficult to prevent than cracks. Pinholes are microscopic paths through which gasses permeated and the WVTR of UHPBF-S decreased. After 1000 h, the areas of the calcium directly under the pinholes in the barriers oxidized and grew in size to cover 20% of the total calcium area which led to a reduction of WVTR ($3.7 \times 10^{-3}$ g m$^{-2}$ d$^{-1}$). D1 defects are related to defects in the coating as a result of particles on the substrate that were too large to be covered with the ORMOCER planarization layers, to particles generated during processing, and/or to damage from local mechanical impact through contact of the barrier layer with rollers or the backside of the next film layer when up winded onto a roll.[49] These defects create preferred permeation pathways through the coating leading to faster degradation locally. The results in Figures 2 and 3 show that the sealant and the film barriers form a coupled system which protects the calcium from degradation. Thus, the performance of the encapsulant does not only depend on the WVTR of the barrier film but also on the handling of the barrier, the sealing method and on the adhesion between barrier and glue as well as that between glue and underlying sample.

2.4. Encapsulation of Perovskite Solar Cell with Permeation Barriers and Their Influence on Degradation Rates

PSCs are not stable when exposed to long term environmental factors including temperature, light, oxygen, and moisture.[37,60–65] Perovskite solar cells must be protected from water because it reacts with CH$_3$NH$_3$PbI$_3$[66–68] hydrating it according to reactions in Equations (1) and (2).[67]

\[
\begin{align*}
&n[\text{CH}_3\text{NH}_3\text{PbI}_3] + \text{H}_2\text{O} \rightarrow [\text{CH}_3\text{NH}_3\text{PbI}_3]^\text{n+1} \\
&[\text{CH}_3\text{NH}_3\text{PbI}_3]^\text{n+1} + \text{H}_2\text{O} \rightarrow \text{PbI}_2 + \text{CH}_3\text{NH}_2 + \text{HI} + \text{H}_2\text{O} + (n-1)[\text{CH}_3\text{NH}_3\text{PbI}_3]
\end{align*}
\]

Frost et al.[67] proposed different degradation mechanisms induced by water where one molecule is enough to initiate the decomposition of CH$_3$NH$_3$PbI$_3$. Interaction with water has a direct impact on the photovoltaic performance when it leads to decomposition of the perovskite in PbI$_2$, CH$_3$NH$_2$, and HI (Equation (2)).

In order to gauge the influence of the barrier/sealant systems and their WVTR on the degradation rates of the solar cells we conducted a lifetime test in which PSCs were kept in dark at constant room temperature and humidity between measurements, that avoid light-induced[60–63] and temperature degradation[64,65] effects (in order to have the same conditions to those of the tests we carried out on our Ca sensors). PSCs were encapsulated using the same barriers described previously, that is, with nothing, glass, PET and UHPBF-S, and the SY-QS bicomponent epoxy resin. Figure 4a presents the evolution of PCE through time for encapsulated and unencapsulated PSCs. Degradation of PSCs over hundreds of hours with a PET-only barrier (high permeation) was only marginally better than equivalent devices without encapsulation. After 840 h, the PCE had dropped to only 6% of its initial value. Instead, PSCs protected by high-performance permeation barriers, that is, glass and UHPBF-S, retained 91% and 76.6%
of their PCE for more than 840 h respectively. These barriers were thus much more successful in blocking oxygen/water permeation with degradation in these encapsulated cells likely mainly due to intrinsic causes such as traps, ion migration, and/or interface instability as well as residual moisture and/or non-complete absence of microscopic pinholes in the UHPBF. After the much longer period of 4344 h the average PCE values were measured to be 60% and 30% of the initial values for glass and UHPBF-S indicating the effect of water and oxygen ingress. For glass ingress occurs laterally mainly through the resin and at its interfaces. Although the averages were lower, the large error bar on the UHPBF-S for the last data point indicates that in the best case PCE values approached those for glass even after such a long test, but the gap and reproducibility over many samples of the flexible barriers can be improved by minimizing pinholes and defects during fabrication, handling, application and gluing procedures. Whereas glass is still the most effective barrier for solar cells, the transparent UHPBF film enables the manufacture of solar cells on flexible substrates.

Our systematic study on WVTRs of barrier/sealant systems and on degradation of perovskite solar cells over time enabled us to extract a phenomenological relation between the two rates, that is, the influence of the performance of barriers on the lifetime of the photovoltaic cells. The degradation rates in PCE of the PSCs were first determined by linear fitting of the shelf-life plots in Figure 4a, and were then plotted as a function of the estimated WVTRs (see Section 4) of the corresponding barrier/adhesive systems in Figure 4b. We applied a Hill sigmoid function for fitting the curve. This is because at very low WVTRs, PCE degradation rates (0.17–0.28% d$^{-1}$) depend on intrinsic effects or residual moisture from fabrication as well as side ingress, so these will tend to dominate over the small amount of moisture leaking in from the barriers. Instead, at the other end of the spectrum (i.e., very high WVTRs), degradation and moisture diffusion will be limited by that occurring through the device (through the electrodes and layers) leading to saturation of the curve which we found to be roughly 3% of relative decrease in PCE per day. We applied the Hill function (Equation (3)) that relates the velocity of one phenomenon (PCE degradation) to the concentration of an external agent (in this case moisture).

$$\text{DR} \text{[\% d}^{-1}\text{]} = \frac{\text{DR}_{\text{max}} \times \text{WVTR}^n}{(\text{WVTR}_{\text{ISO}})^n + \text{WVTR}^n}$$  

where DR stands for degradation rate of the PCE of the solar cells, DR$_{\text{max}}$ for the maximum DR which corresponds to the rate measured for the sample without encapsulation (data point at DR = 2.98% d$^{-1}$ in Figure 4b), WVTR$_{\text{ISO}}$ for the WVTR value when DR is 50% of DR$_{\text{max}}$ and n is the Hill coefficient which controls the sigmoidicity of curve. The constant WVTR$_{\text{ISO}}$ = 6.7 × 10$^{-3}$ g m$^{-2}$ d$^{-1}$ indicates the WVTR of an encapsulation barrier needed to protect a PSC from moisture and slow down the degradation speed by half compare with unencapsulated PSCs. With the phenomenological relation between degradation rates of perovskite solar cells as a function of the WVTR of the barrier/adhesive systems utilized for their protection we extracted from our systematic investigations, one is able to gauge the influence of the latter on the former. For example, starting from the non-encapsulated case (WVTR = 10$^3$ g m$^{-2}$ d$^{-1}$) an improvement by three orders of magnitude of the WVTR (e.g., WVTR = 0.1 g m$^{-2}$ d$^{-1}$ which is representative of a PET barrier with an additional 15 nm of protective Al) would reduce degradation rates by 74%. Instead, a barrier/sealant improvement (WVTR) of two orders of magnitude, but from 10$^2$ to 10$^{-3}$ g m$^{-2}$ d$^{-1}$, would lead to a much greater reduction of 97% in degradation rates of PCE, lowering it down to 0.09% d$^{-1}$. An additional factor of 100–1000 (very low WVTRs between 10$^{-5}$ and 10$^{-8}$ g m$^{-2}$ d$^{-1}$) would then pull down solar cell degradation rates down to the values of 0.007% and 0.002% d$^{-1}$ respectively. Therefore, to reduce the DR of PSCs and retain about 80% of their initial PCE for at least a 3 year period, it is recommended that either a barrier/sealant system with a WVTR of or below 10$^{-5}$ g m$^{-2}$ d$^{-1}$ is applied or that more stable perovskite and transport layers are utilized as well as the level of intrinsic moisture during fabrication procedures of devices is reduced to a minimum. Low WVTR values (i.e., < 10$^{-6}$) will have a relative impact in DR compared with the high cost of fabrication necessary to reach these ultra high levels. These trends can be useful for developers of encapsulation barriers, materials scientists and device engineers on how to direct efforts to improve intrinsic stability of PSCs together with the cost to performance ratio of barriers aimed at finding the most effective solution for encapsulation of solar cells in terms of both cost and photovoltaic performance over time. One must also consider that this trend between DR and WVTR can be different when employing other encapsulation systems (e.g., lateral sealings), PSC architectures (e.g., PSC with p-n structure), different test conditions (e.g., with high temperatures, humidity and/or irradiance), and different barrier structures and adhesives. Furthermore, future studies may focus on gauging encapsulation barriers and PSCs with accelerated tests including the ISOS-D-3 damp heat test (T = 85 °C and RH = 85%) or even in real outdoor conditions.

3. Conclusions

We evaluated polyethylene terephthalate (PET), flexible ultra-high permeation barrier films (UHPBF), and rigid glass as encapsulation barriers for perovskite solar cells. The performance of flexible UHPBF strongly depends on barrier orientation, manipulation and storage. The UHPBF must be kept in an inert atmosphere (N$_2$ or Argon) or dried before their application because barriers absorb water and oxygen which can be released into devices when they are encapsulated and operated. Also, barriers must adhere ensuring a homogeneous coverage of resin/adhesive, for example by using a non-stick film when applying pressure to do so uniformly upon lamination. By doing so, the onset of barrier defects (i.e., pinholes and cracks) can be minimized. The addition of an SiO$_x$C$_y$H$_z$ layer on the multilayer stack of UHPBFs increased the adhesion between UHPBF and cured resin sealant when applied on calcium test samples which reduced the interface diffusion and improved the WVTR of the barrier/adhesive system from 5.7 × 10$^{-3}$
to $8.2 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$. The encapsulated samples with the UHPBF with SiO$_2$C$_x$H$_y$ (labelled UHPBF-S) showed a drastically improved WVTR compared to those encapsulated with a plain PET film (i.e., $4.4 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$) and were closer to those with glass (i.e., $1.9 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$) but being flexible, light-weight, and compatible with R2R lamination processes. Additionally, barriers were also tested for the encapsulation of PSCs. The PSC encapsulated with PET lost 36% of its initial PCE after 696 h but fell drastically to 0 in the next 150 h. The optimal UHPBF-S retained 77% of its initial PCE after 840 h. As a comparison, that encapsulated with glass retained 91% of its PCE after 840 h only 14% higher than UHPBF-S. After more than 4344 h, the drop was more significant: PSCs encapsulated with UHPBF-S and glass retained on average 30% and 60% of initial PCE (in relative terms). We were able to extract an empirical mathematical relationship between the permeation rate of barriers (i.e., WVTR values) and the degradation rate (DR) of perovskite solar cells based on the results obtained by electrical calcium test and shelf-life tests of solar cells, respectively. The DR falls exponentially when the WVTR of the encapsulation barrier/sealant decreases from $10^4$ to $10^3$ g m$^{-2}$ d$^{-1}$. Outside that range any gains or losses are mitigated by the tailoring of the S-shaped curve relating the two parameters. The information garnered with these systematic studies of barrier/device systems is expected to be of help to those developing encapsulation strategies for large area electronic devices and to those developing rigid and flexible solar cells as well as to the development of new encapsulation barriers and sealant systems. Nevertheless, we consider that different encapsulation setups (i.e., lateral sealing), PSC architecture (i.e., inverted p-i-n structure, or the use of durable materials), barrier structures (new developments), and test conditions (i.e., different temperatures, humidity and irradiation) will affect the relationship between DR of encapsulated solar cells and WVTR of barriers. Thus, future investigations can focus on testing both barriers and solar cells under several critical conditions such as high temperatures and high humidity, to determine how the DR/WVTR trend depends on the external environmental, barrier/sealant systems and internal effects such as traps, ion migration, and/or interface instability.

4. Experimental Section

**Calcium Test Samples:** Figure 1a shows the schematic design of devices implemented for both optical and electrical calcium tests (Ca-Test). The top view shows five calcium sensors (gray rectangle), each placed between two ITO electrodes (light blue rectangle), and the barrier (size and position) under test (purple dash line). The cross-sectional view presents the layer-by-layer design of the calcium test devices. First, the glass/ITO substrate (Kintec, 8 µm) was patterned by wet etching (HBr solution at 100 °C by 10 min) and cleaned sequentially in an ultrasonic bath with acetone, ethanol, and 2-propanol, each for 10 min. Then, samples were transferred to a metal evaporator and 250 nm thick 1.0 × 0.15 cm$^2$ stripes of calcium (Sigma-Aldrich, 99.9%) were evaporated at pressures in a range from $5 \times 10^{-4}$ to $1 \times 10^{-6}$ mbar. The barriers were dried beforehand at 80 °C in an N$_2$ environment (glove box) for 6 h to remove any moisture. To ensure a minimum distance of 5 mm from Ca-sensor to barrier edge in all directions, the barriers were cut to a 2.0 × 2.4 cm$^2$ size. Finally, the barrier was pressed over the sample with an anti-stick PTFE rectangular slab which allowed to apply the barrier to the substrate via UV-VIS curable resin (Ossila E131) uniformly. To avoid excess of resins on the edge, (40 ± 10) mg of resin was applied. The area close to the edge was covered with a common electrical tape (black tape) stripe to prevent aggregation of resin around the edge. Once the resin was cured the tape was removed with the resin that was on it. This procedure produced very clean edges. Lateral sealing or getters were not applied at the edges. Tested barriers are shown in Figure 1b: Melinex ST506 PET film (175 µm), glass microslide (1.1 mm) and ultra-high permeation barrier system provided by the Fraunhofer Institutes for Electronic Beam and Plasma Technology (FEP), Silicate Research (ISR), and Process Engineering and Packaging (IVV) within the Fraunhofer POLO alliance. The encapsulation was carried out inside the glove box and the resin was applied on the multiple oxide/ORMOCER stack of ultra-high permeation barrier. In case of PET and glass, there was no preferential side for resin application.

**Ultra-High Permeation Barrier Films:** The ultra-high permeation barrier films (UHPBF) were prepared as reported previously.[42,43] The structure of the first tested barrier[28] (labelled as UHPBF-R), was PET (Melinex 401 CW, 75 µm)/ZTO (zinc-tin-oxide Zn$_2$SnO$_4$, 180 nm)/ORMOCER (organic-inorganic hybrid polymer,[44] 1 µm)/ZTO(180 nm). A second barrier structure was tested (labelled as UHPBF-S). That structure was based on a DuPont OPTFINE PQA1 polyethylene naphthalate (PEN) film which has lower surface roughness and less defects compared to Melinex 401. Furthermore, the UHPBF-S stack included more than two ZTO layers (but lower layer thickness), and the addition of a silicon plasma polymer (SiO$_2$C$_x$H$_y$) top layer which improved the barrier-resin adhesion: PEN (125 µm)/ZTO (50 nm)/ORMOCER (1 µm)/ZTO (50 nm)/ORMOCER (1 µm)/ZTO (50 nm)/SiO$_2$C$_x$H$_y$ (50 nm). The SiO$_2$C$_x$H$_y$ layer was deposited in a dual magnetron reactive sputter deposition (Ti-Targets, $2 \times 900 \times 120$ mm) at 10 kW total plasma power in an HMDSO/Oxygen atmosphere with an HMDSO to Oxygen ratio of 1:2 leading to an amorphous polymer coating with a chemical composition similar to PDMS. More details on that process can be found in.[83] The scanning electron microscopy (SEM) of both UHPBF-R and UHPBF-S barriers are shown in Figure 1c.d.

**Barrier Characterization:** The thickness of resin was measured using a digital thickness gauge meter (Käfer) with a resolution of 1 µm. The performance of the sealant/barrier was investigated utilizing the calcium test configuration of Figure 1a. The WVTR and OTR can be extracted from calcium tests; however, for a calcium test carried out in ambient environment, the effect of oxygen in the degradation of calcium is negligible compared to that of water.[50] Therefore, it is the WVTR that is extracted from calcium tests. Calcium oxidation allows the estimation of WVTR on encapsulated samples because gray-color/conductive calcium sensors become transparent/insulating when oxygen or water molecules interact with calcium atoms producing CaO and Ca(OH)$_2$ compounds.[52,85] The Ca-test was configured with a two-wire setup using an ohmmeter with an error of ±10% of the reading. The ohmmeter reading represented the sum of calcium sensor and ITO electrodes resistance; thus, to eliminate the contribution of the ITO and its contact resistance, the resistance values were normalized to that of the pristine calcium strip only which was calculated using the experimental value of resistivity, $\rho = 8.95 \times 10^{-8}$ Ω m.[32] In the case of the optical Ca-test, the image (photographs) of the Ca sensors were captured by a 16 MP CCD camera with a backside illumination CMOS sensor, focal length of 4.3 mm and focal aperture of f/1.9. The color pictures were converted to black and white and filtered with a nine-pixel window to avoid noise and shadows using the MatLab Image Processing Toolbox. The white pixels represented the area covered with metallic calcium and the black ones empty space and calcium that had become oxidized (typically under encapsulation defects including pinholes, cracks, and trapped gas as well as from lateral permeation). Image processing measured the area of calcium sensor in pixels; therefore, to quantify the calcium area reduction was necessary to define a proportionality constant between pixel and mm$^2$ which was calculated.
experimentally, and its value was $8.3 \times 10^{-4}$ mm$^2$ per pixel. Additionally, before any measurement, a sample with chromium strip (instead of calcium) was used as reference. The optical calcium test also enables to identify and monitor degradation paths and mechanisms.

The results of optical (change in area including deposition defects) and electrical (change in conductance) Ca-test were plotted as a function of time, and the resulting curves were fitted with the quick fit tool of Origin from OriginLab Company. Fitting was performed on the linear part of the curve and the calculated slope corresponded to the terms of Equations (4) and (5) respectively.

$\frac{\partial d}{\partial t} = -2 \left( \frac{M_{H2O}}{M_{Ca}} \right) \frac{d(A)}{\rho_o}$ (4)

$\frac{\partial (1/R)}{\partial t} = -2 \left( \frac{M_{H2O}}{M_{Ca}} \right) \frac{d(1/R)}{\rho_o}$ (5)

where $A$, $R$, $\rho$, $d$, $\rho_o$, $M_{Ca}$, and $M_{H2O}$ are the area, resistance, density, resistivity, thickness, initial area, initial length, and initial width of calcium sensor, and $M_{Ca}$ and $M_{H2O}$ are the molecular weights of water and calcium.

The error of fitting permitted to establish a range of WVTRs which are reported in Table 1.

**Perovskite Solar Cell Fabrication:** All solvents and reagents, if not specified, were purchased from Sigma-Aldrich and used as received. The evaluated PSC had the n-i-p planar structure (glass/ITO/SnO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Au) presented in Figure 1b. The fabrication started with the patterning of the glass/ITO (Kintec, 8 $\Omega$ sq$^{-1}$) following the same methodology used for calcium test samples. The SnO$_2$ electron transport and compact blocking layer (SnO$_2$-2H$_2$O 0.1 m in ethanol) was deposited on glass/ITO substrate by two steps spin-coating process (1500 rpm for 30 s, and 2500 rpm for 30 s) followed by an annealing at 150 °C for 1 h in air. Then, the perovskite (CH$_3$NH$_3$PbI$_3$) solution compounded by PbI$_2$ (TCI, 99.999%):MAI with 1:1 molar ratio and dissolved in DMF:DMSO (9:1, v:v), to obtain a final concentration of 1.4 $\times$ 10$^{-3}$ M, was spin coated on the SnO$_2$ layer using the solvent engineering method as reported in.[87] Briefly, the CH$_3$NH$_3$PbI$_3$ was deposited in a two steps spin coating deposition consisting of 1000 rpm for 10 s, followed by 5000 rpm for 45 s. Once 35 s of spin remained, 0.7 mL of diethyl ether solvent were dropped on the rotating substrate to obtain a transparent perovskite films that became black after annealing at 50 °C for 2 min and 100 °C for 10 min. Next, the Spiro-OMeTAD hole transport layer (Borum New Material Technology Ltd, 73.5 mg mL$^{-1}$ in chlorobenzene) doped with TBP (26.7 $\mu$L mL$^{-1}$), LiTFSI (16.6 $\mu$L mL$^{-1}$), and cobalt(III) complex (7.2 $\mu$L mL$^{-1}$) was spin coated on perovskite film at 2000 rpm for 20 s. Finally, the gold (Au) back electrode was thermally evaporated at a pressure below 10$^{-4}$ mbar. In the evaporation, a shadow mask was used allowing the appropriate patterning of devices enabling the fabrication of 8 different devices per substrate each with a 0.1 cm$^2$ area (see Figure 1b). The PSCs were encapsulated in an N$_2$ atmosphere with the barriers (glass, PET, or UHPBF-S) following the same procedure used for Ca-test samples. PSCs were encapsulated using an epoxy resin (Pacer Technology, SY-QS) as sealant and following the same procedure for Ca-Test samples. This is because the UV-curable Ossila, the barriers (glass, PET, or UHPBF-S) following the same procedure of the solar cell (power conversion efficiency—PCE, current density—$I_{sc}$, open-circuit voltage $V_{oc}$, and fill factor—FF) were measured with a Keithley 2420 source meter under standard test conditions (STC): 1 sun illumination (AM1.5G Class A ABET solar simulator (1000 W m$^{-2}$) calibrated with an EKO MS-602 Pyranometer) at room temperature (25 °C). Measurement started with voltage step, scan speed, and delay time of 20 mV, 1 s, and 200 ms respectively. The shelf life test was used to monitor the time evolution of photovoltaic parameters of PSCs. Shelf life tests for PSCs were carried out according to the ISOS-D-1 protocol. The PSCs were kept in dark (no light source) at ambient temperature and relative humidity (RH) between measurements. Here, the shelf life test (T = 25 °C and RH = 35%) were carried out for 4344 h. The WVTRs used in Figure 4b are those from Table 1 relative to the different encapsulation barrier multiplied by an experimental factor since we utilized the bicomponent resin rather than the UV-curable one for encapsulation of the cells. The latter chemically reacted with spiro-OMeTAD layer and traces of DMSO in CH$_3$NH$_3$PbI$_3$ in the cells whereas the former often reacted with the Ca sensors, probably caused by traces of chemicals arising from the reaction between the two components, leaving only a sporadic number of sensors working. Thus, to draw the important relationship between cell degradation rate and WVTR of the encapsulation system we extracted the multiplication factor from those glass-encapsulated calcium sensors that did not initially fail upon application of the bicomponent. Notwithstanding the large error on WVTRs, the fact that the x-scale of Figure 4b is over many orders of magnitudes still make the quantitative trends definitely significant (see inset of Figure 4b for fitting values and errors).

**Acknowledgements**

This project received funding from the Departamento del Huila’s Scholarship Program No. 677 from Huila, Colombia, from the European Union’s Horizon 2020 research and innovation programme under grant agreement no. 763989 APOLO, and from the Italian Space Agency (ASI) for project PEROSKY-Perovskite and other printable materials for energy application in space (no. 2018-1-R.0). The article reflects the views of the authors, and the funding agencies are not responsible for any use that may be made of the information that it contains. The authors thank the Fraunhofer Institutes FEP, ISC, and IVV for providing the different ultra-high permeation barriers which were fabricated within the Fraunhofer POLO alliance. The authors thank Matteo Gasbarri, Alessandro Palma, Luca La Notte, Fabio Matteocci, Emanuele Calabro, Aldo Di Carlo, Andrea Reale, and Francesca Brunetti for useful discussions.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

adhesive resins, barrier films, degradation rates, encapsulation, lifetime, sealing, stability

Received: December 27, 2018

Revised: May 30, 2019

Published online: August 14, 2019

1. W. Zhang, G. E. Eperon, H. J. Snaith, Nat. Energy 2016, 1, 16048.
2. Y.-S. Yian, J. Photonics Energy 2011, 1, 011009.
3. C. J. Brabec, Sol. Energy Mater. Sol. Cells 2004, 83, 273.
[62] N. N. Shlenskaya, N. A. Belich, M. Grätzel, E. A. Goodlin, A. B. Tarasov, J. Mater. Chem. A 2018, 6, 1780.

[63] W. Nie, J.-C. Blancon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, S. Tretiak, J. J. Crochet, G. Gupta, A. D. Mohite, Nat. Commun. 2016, 7, 11574.

[64] G. Divitini, S. Cacovich, F. Matteocci, L. Cinà, A. Di Carlo, Nat. Energy 2016, 1, 15012.

[65] Y. Han, S. Meyer, Y. Dkhissi, K. Weber, J. M. Pringle, U. Bach, L. Spiccia, Y.-B. Cheng, J. Mater. Chem. A 2015, 3, 8139.

[66] J. A. Christians, P. A. Miranda Herrera, P. V. Kamat, J. Am. Chem. Soc. 2015, 137, 1530.

[67] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, A. Walsh, Nano Lett. 2014, 14, 2584.

[68] G. Niu, X. Guo, L. Wang, J. Mater. Chem. A 2015, 3, 8970.

[69] J. P. Correa Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. Srimath Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, A. Hagfeldt, Energy Environ. Sci. 2015, 8, 2928.

[70] M. Saliba, M. Stolterfoht, C. M. Wolff, D. Neher, A. Abate, Joule 2018, 2, 1019.

[71] A. Guerrero, J. You, C. Aranda, Y. S. Kang, G. Garcia-Belmonte, H. Zhou, J. Bisquert, Y. Yang, ACS Nano 2016, 10, 218.

[72] S. Ito, S. Tanaka, K. Manabe, H. Nishino, J. Phys. Chem. C 2014, 118, 16995.

[73] A. L. Palma, L. Cinà, S. Pescetelli, A. Agresti, M. Raggio, R. Paolesse, F. Bonaccorso, A. Di Carlo, Nano Energy 2016, 22, 349.

[74] Q. Dong, F. Liu, M. K. Wong, H. W. Tam, A. B. Djurišić, A. Ng, C. Surya, W. K. Chan, A. M. C. Ng, ChemSusChem 2016, 9, 2518.

[75] N. Ahn, K. Kwak, M. S. Jang, H. Yoon, B. Yang, J. K. Lee, P. V. Pikhitsa, J. Byun, M. Choi, B. Y. Lee, J. K. Lee, P. V. Pikhitsa, J. Byun, M. Choi, Nat. Commun. 2016, 7, 1.

[76] D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, J. Mater. Chem. C 2018, 6, 162.

[77] Z. Ahmad, M. A. Najeeb, R. A. Shakoor, A. Alshrafi, S. A. Al-Muhtaseb, A. Soliman, M. K. Nazeeruddin, Sci. Rep. 2017, 7, 15406.

[78] F. Di Giacomo, A. Fakharuddin, R. Jose, T. M. Brown, Energy Environ. Sci. 2016, 9, 3007.

[79] J. Adams, M. Salvador, L. Lucera, S. Langner, G. D. Spyropoulos, F. W. Fecher, M. M. Voigt, S. A. Dowland, A. Osvet, H. J. Egelhaaf, C. J. Brabec, Adv. Energy Mater. 2015, 5, 1.

[80] J. N. Weiss, FASEB J. 1997, 11, 835.

[81] S. Goutelle, M. Maurin, F. Rougier, X. Barbaut, L. Bourguignon, Fundam. Clin. Pharmacol. 2008, 22, 633.

[82] A. A. Sabouri, A. A. Moosavimovahedi, Biochem. Educ. 1994, 22, 48.

[83] S. Günther, M. Fahlund, J. Fahleiteh, B. Meyer, S. Straach, N. Schiller, Thin Solid Films 2013, 532, 44.

[84] K. H. Haas, Adv. Eng. Mater. 2000, 2, 571.

[85] P. O. Nilsson, G. Forssell, Phys. Rev. B 1977, 16, 3352.

[86] R. Kumar, M. Auch, E. Ou, G. Ewald, C. S. Jin, Thin Solid Films 2002, 417, 120.

[87] N. Ahn, D.-Y. Y. Son, I.-H. H. Jang, S. M. Kang, M. Choi, N.-G. G. Park, J. Am. Chem. Soc. 2015, 137, 8696.

[88] M. O. Reese, S. A. Georgygan, M. Jørgensen, E. Bundgaard, S. R. Kurtz, D. S. Ginley, D. C. Olson, M. T. Lloyd, P. Morvillo, E. A. Katz, A. Elschner, O. Haillant, T. R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K. R. Kirov, G. Trimml, T. Rath, O. Ingaräns, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuinness, S. (Jimmy) Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D. M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, Sol. Energy Mater. Sol. Cells 2011, 95, 1253.