

Understanding moisture ingress and packaging requirements for photovoltaic modules

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This paper first appeared in the fifth print edition of *Photovoltaics International* journal.

ABSTRACT

Outside of the challenges of fabricating state-of-the-art photovoltaic devices, further care must be taken to package them such that they can withstand environmental conditions for an accepted lifetime of 20-plus years. Moisture ingress is a big adversary to hermetic packaging. The diffusion of water through barriers and edge seals can be minimized by careful choice of materials and package/barrier architecture. However, at present, there exist no solutions for extremely water-sensitive materials for flexible applications. Presented in the following is a review of the physics of permeation, the means of measuring permeation, current architectural strategies for semi-hermetic packages, and a brief evaluation of some common encapsulant materials.

Packaging schemes are often described as 'hermetic'; however, other than airtight, no quantitative definition apparently exists. For foodstuffs with little sensitivity to moisture, airtight means something very different than when describing photovoltaic modules. Even glass/

glass and metal/glass seals that are often considered hermetic have some permeation, but on a geologic timescale for molecules like water. For any system in which leakage can be measured, but is on the order of the desired lifetime, the term 'semi-hermetic' is perhaps more appropriate.

“As moisture can cause significant degradation, it is important to understand the physics of its ingress.”

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When examining packaging requirements, the time over which the package needs to succeed in preventing ingress must be defined, as well as what contaminants should be excluded. It is important to separate steady-state behaviour from transient response. In this paper, the term 'semi-hermetic' will be used to describe systems in which effectively all moisture is excluded for at least 20 years. As moisture can cause significant degradation, it is important to understand the physics of its ingress together with the terms that describe it, general packaging strategies to limit it, how to appropriately measure it, and the limits of commonly used materials. This article will touch on each of these, while referring the interested reader to more in-depth reviews where appropriate.

Fickian physics, WVTR, lag time and breakthrough time

Moisture ingress is inherently a diffusion problem. In PV modules, moisture may diffuse both through the barrier and the edge seal (Fig. 1). Designing a module to make it semi-hermetic requires knowing information about the barrier and the sealants used. Some properties are material dependent like diffusivity and solubility, while others depend on how they are incorporated into a module design (e.g. physical dimensions and how they are dried prior to use) like water vapour transmission rate (WVTR), breakthrough time (t_b), and lag time (t_{lag}).

Diffusivity (D) is defined as the proportionality constant between the gradient in the moisture's concentration field (∇C) and the flux (J) as

$$J = -D\nabla C \quad (1)$$

The change in concentration with time is thus represented as

$$\frac{\partial C}{\partial t} = -\nabla J = (D\nabla^2 C) \quad (2)$$

If the diffusivity of a material is not dependent on concentration, the material is referred to as Fickian, which simplifies Equation 2 as

$$\frac{\partial C}{\partial t} = -\nabla J = (D\nabla^2 C) \quad (3)$$

In the special case of permeation of water through a thin membrane, the flux is one-dimensional and is referred to as the water vapour transmission rate. Assuming a Fickian material, the WVTR, as a function of time, through an initially dry membrane that is dry on one side and held at a constant concentration (C_s) on the other, can be modelled as [1-3]

$$WVTR(t) = \frac{DC_s}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \right] \quad (4)$$

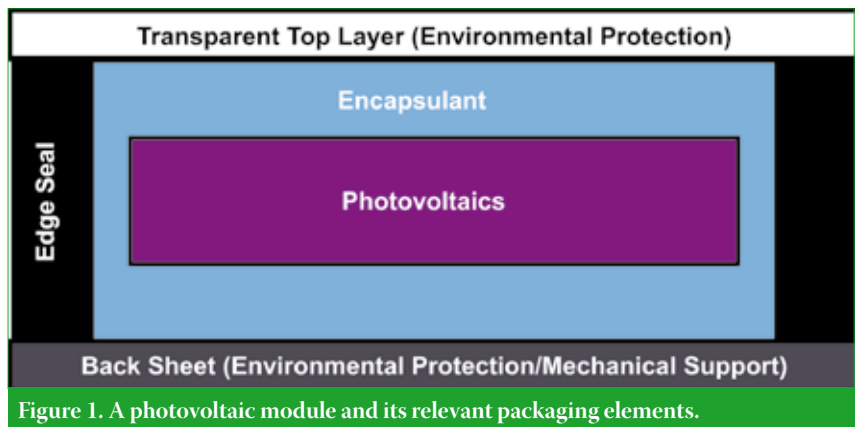


Figure 1. A photovoltaic module and its relevant packaging elements.

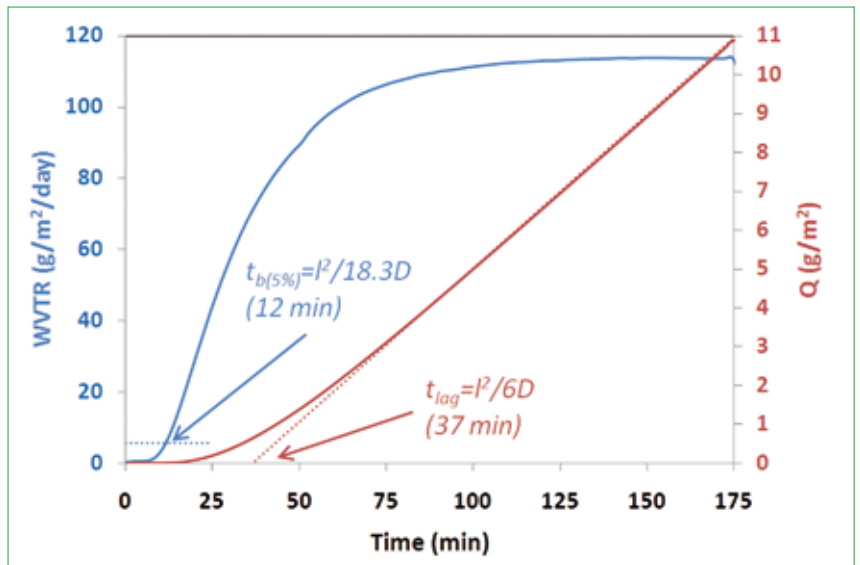


Figure 2. Graphical representation of transient breakthrough and lag time for a 2.84mm-thick EVA film at 85°C with saturated water vapour on one side and dry N_2 on the other.

$$Q(t) = \int_0^t WVTR(t) dt = \frac{DC_s}{l} t - \frac{l C_s}{6} - \frac{2l C_s}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{l^2}\right) \quad (5)$$

where t is time and l is the thickness of the membrane. Similarly, the total amount of permeate (Q) as a function of time can be modelled as [4].

Inspection of Equations 4 and 5 indicate that there is a delay before significant moisture begins to permeate a membrane, followed by a steady state condition (Fig. 2). In both cases, the steady state condition is determined by the value of the ratio DC_s/l , and the characteristic time for these processes is given by D/l^2 . When $Q(t)$ is measured, a line drawn through $Q(t \rightarrow \infty)$ intercepts the time axis at a time called the lag time (t_{lag}) which is related to the diffusivity by

$$t_{lag} = \frac{l^2}{6D} \quad (6)$$

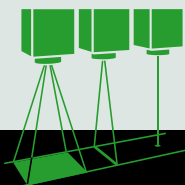
When $WVTR(t)$ is measured, the characteristic time can be related to the breakthrough time (t_b), which is the time taken to reach 5% (or any other desired number) of the steady state WVTR, by

$$t_b = \frac{l^2}{18.3D} \quad (7)$$

Thus, the breakthrough time describes the time required for moisture to begin permeating significantly.

Edge seals

Edge seal materials consisting of a low-diffusivity material with desiccant are being investigated and developed by several manufacturers. These materials are typically used with impermeable front- and back-sheets (typically glass) which restrict moisture ingress to the edge of the modules and through the J-box (Fig. 3). Because permeation through the edge seals is essentially a 1-D diffusion process,



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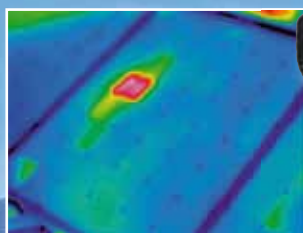
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similar to the permeation through a membrane, the breakthrough time for a PV module edge seal can be determined by replacing l^2 with the width of the edge seal (w^2). For non-Fickian materials, often with fillers and desiccants, this breakthrough time is related to the diffusivity and width of an edge seal by [1, 5]

$$t_{b,NF} = K \frac{w^2}{D} \quad (8)$$

where K is a material-dependent constant [6].

Some PV modules do not use glass or metal foil as front- and back-sheets (barriers), in which cases the permeation of the barrier must be taken into account. Assuming uniform moisture concentration in the encapsulant (requiring the encapsulant's diffusivity to be much greater than the barrier's), and that the WVTR across the barrier is related to the change in concentration $\Delta C = C_{E,Sat} - C_E$, then the moisture concentration changes as a function of time as

$$\frac{dC_E}{dt} = \frac{WVTR_{B,Sat}}{C_{E,Sat} l_E} (C_{E,Eq} - C_E) \quad (9)$$

where B refers to barrier, E refers to encapsulant, and Sat refers to saturated conditions. Integrating Equation 9 yields the water content as a function of time of an initially dry module exposed to fixed environmental conditions

$$\frac{C(t)}{C_{E,Eq}} = 1 - \exp\left[-\frac{WVTR_{B,Sat} t}{C_{E,Sat} l_E}\right] \quad (10)$$

From this, we can obtain the characteristic half-time for equilibration of [2].

$$\tau^{1/2} = 0.693 \frac{C_{Sat,E} l_E}{WVTR_{B,Sat}} \quad (11)$$

For example, typical values for EVA have $C_{Sat} = 0.0021 \text{ g/cm}^3$ at 25°C with $l = 0.46 \text{ mm}$. This leads to the product $C_{Sat,E} l_E \cong 1 \text{ g/m}^2$. Thus, back-sheet materials with WVTR's $\sim 1 \text{ g/m}^2/\text{day}$ lead to an equilibration half-time of 17 hours. To achieve an equilibration half-time of 20 years (at 25°C) requires a WVTR $< 10^{-4} \text{ g/m}^2/\text{day}$. If a WVTR this low is achieved, ingress through the edge seal becomes a concern. To put these numbers into perspective, a 1 m^2 section of a material with a WVTR of $1 \text{ g/m}^2/\text{day}$ will see enough water diffuse into it each day to create a $1 \mu\text{m}$ -thick layer of water over the entire square meter. Assuming that the water continues to collect (fortunately the water also diffuses out), by the end of 20 years this results in more than 7.3 litres of water. A material with a WVTR of $10^{-4} \text{ g/m}^2/\text{day}$ would collect approximately a $1 \mu\text{m}$ -thick water layer (or 0.73ml) after

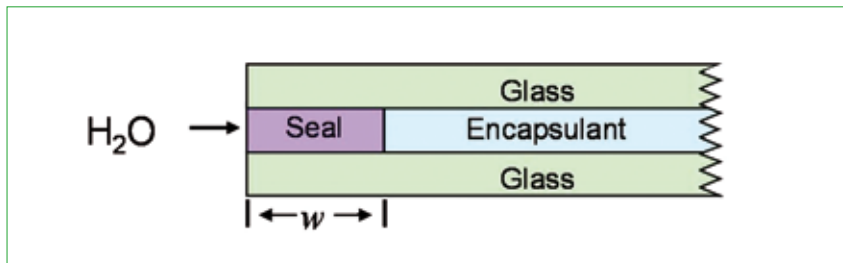


Figure 3. Schematic diagram of the edge of a module using a very low permeability edge seal to keep out moisture.

20 years and a material with a WVTR of $10^{-6} \text{ g/m}^2/\text{day}$ would result in an approximately 10 nm -thick layer (or $7.3 \mu\text{l}$).

Packaging strategies

To create a semi-hermetic package, generally an approach like that shown in Fig. 1 must be used. There are four separate packaging elements: the encapsulant, the edge seal, and the front- and back-sheets. Standard encapsulants like EVA without an edge seal are incapable of creating a semi-hermetic package due to their high diffusivity and low solubility [7]. For instance, to achieve a 20-year, 10% breakthrough time with EVA at 40°C , a width of $\sim 100 \text{ cm}$ would be necessary. In order to extend the breakthrough time to multiple decades while maintaining reasonable widths, poly-isobutylene (PIB)-based edge seals have been loaded with desiccant materials like molecular sieve. These effectively increase the solubility of the sealant retaining similar diffusivity in the polymer matrix, while temporarily trapping moisture in the desiccant. Still, semi-hermetic packaging at elevated temperatures and humidity requires significant edge seal width. In real applications, delamination effects that may be accelerated by moisture ingress and UV exposure must also be addressed, as adhesive failure of sealants is a common failure mode.

“PIB-based edge seals effectively increase the solubility of the sealant retaining similar diffusivity in the polymer matrix, while temporarily trapping moisture in the desiccant.”

When a barrier like glass or metal is used with an edge seal, the most likely path of moisture ingress is through the edge seal and the J-box barring any damage to the barrier (Fig. 3). However, as flexible thin-film PV becomes more prominent, especially with its greater sensitivity to moisture/oxygen, flexible barriers with low permeation become

more important unless a breathable back-sheet is desired. Currently there is no polymer-only material that can provide semi-hermetic barrier performance for PV applications ($< 10^{-4} \text{ g/m}^2/\text{day}$).

Strategies attempting to address this problem generally involve the incorporation of inorganics to reduce permeation. Permeation in these systems tends to be defect-dominated by either grain boundaries or pinholes of the inorganic layers [4, 8]. While reducing the defect densities has been attempted, stacks called ‘dyads’ of inorganic/organic materials have also been investigated to decouple defects between inorganic layers and create a ‘tortuous path’ between defects [4]. This not only improves the steady state transmission of the barrier, but can significantly impact the breakthrough time with times of 20 years predicted to be achievable by 12 dyads with a defect spacing of $5 \mu\text{m}$ [4].

Another approach is to deposit the barrier directly on the finished module, typically using a technique like plasma-enhanced chemical vapor deposition (PECVD). While this technique may suffer from the same problems with defects, it does remove the necessity of using any edge seal. Furthermore, if a pinhole develops in the barrier, the extent of the damage may be limited to a much smaller area.

Measurement of moisture ingress

There are a variety of methods that have been developed to quantify water permeation. Each has limitations either in sensitivity, throughput, speed, or capital outlay/cost. In general, they can be divided into two main categories: scavenger and diffusion cell methods. Scavenger methods, such as the calcium test or the gravimetric cup test, quantify the amount of moisture that is absorbed or scavenged by a material then relate it to permeation through $Q(t)$ (see Equation 5). Such tests can be set up in a variety of configurations and use a controlled surrounding environment to regulate the test temperature and relative humidity.

Diffusion cell methods, such as the radioactive tracer method, mass spectrometry method, or the isostatic test, measure the amount of moisture passing through the barrier directly. These

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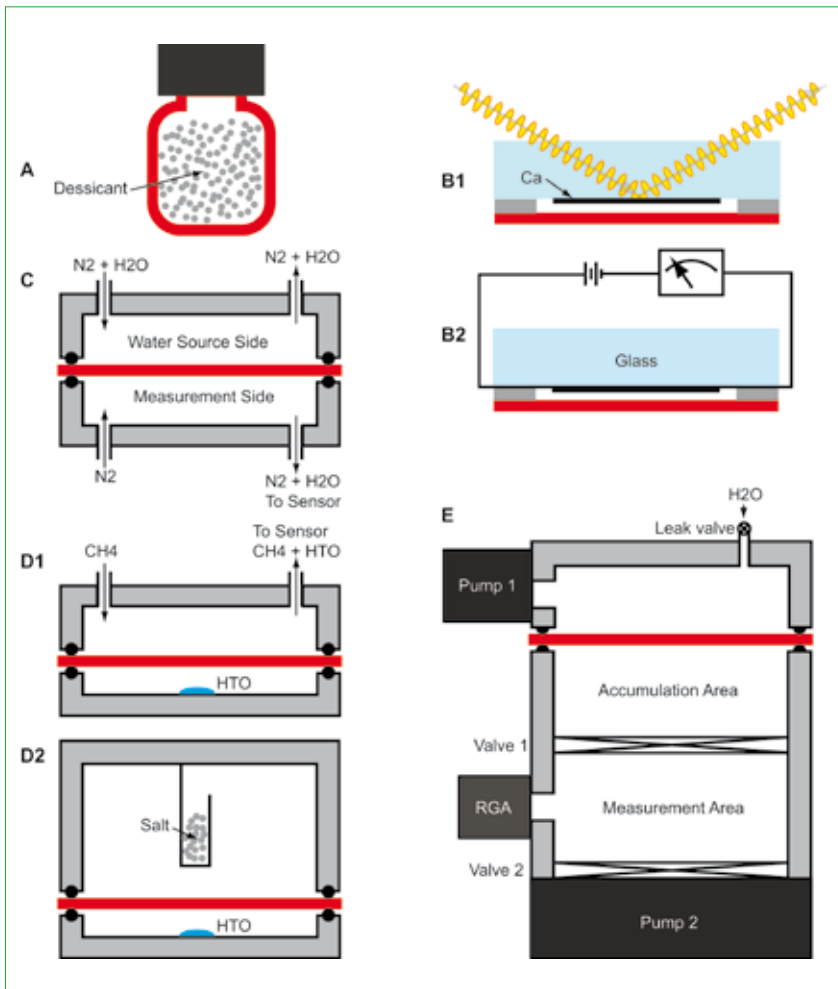


Figure 4. Schema of methods for measurement of WVTR through permeation barriers showing: A- gravimetric cup test; B- calcium test with B1 optical detection and B2 electrical detection; C- isostatic test; D- radioactive tracer test with D1 ionization chamber detection and D2 hydroscopic salt/scintillation detection; and E- mass spectrometry method shown with programmed valving.

tests are all set up similarly with the test barrier layer positioned in the middle of the diffusion cell, separating a water-rich source side from a dry measurement side. The relative humidity is controlled by the amount of water introduced to the source side of the cell, or liquid water may hold the space at 100% RH. Temperature is regulated by heating the diffusion cell. A brief description of these scavenger methods follows, illustrated for each case in the schematics in Fig. 4.

Scavenger methods

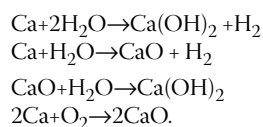
Gravimetric cup test

The most simplistic method of measuring WVTR (ASTM E96), sometimes referred to as the cup test, is used in the packaging industry (Fig. 4A). For these measurements, the test package, comprised of a test barrier material, is filled with a precisely measured mass of desiccant. The package is then sealed and placed in a controlled temperature and humidity environment. After an elapsed time (Δt), the desiccant is removed and mass change (Δm) is recorded. The WVTR is calculated from Δt and Δm (WVTR is assumed constant for Δt). This method is

simple; the temperature and humidity can be easily controlled and many samples can be tested simultaneously. However, the breakthrough time cannot be easily determined from the data. Further, it is impossible to determine if the measured WVTRs are a result of diffusion through the barriers or through the sealed edges. Finally, the lower sensitivity limit of $\sim 0.1 \text{ g/m}^2/\text{day}$ makes this test method unsuitable for PV and OLED barrier testing.

Calcium test

The calcium degradation test method (Ca test) uses a thin Ca layer to scavenge water that passes through a test barrier. There are two basic types of Ca test: an optical (Fig. 4B1) and an electrical method (Fig. 4B2). While the means of determining the amount of Ca degradation are different, the basic principles of the Ca test are the same. This test depends on the absorption of nearby water molecules by the Ca metal film to form CaO or $\text{Ca}(\text{OH})_2$ via



While the relative rate of reaction between water and oxygen, to the authors' knowledge, has not been quantified at elevated temperatures, at ambient temperatures the rate of oxygen reaction relative to water is negligible as determined by isotopic labelling methods [9]. For the test assembly, a thin film of Ca metal is deposited by evaporation or sputtering onto the backside of the test barrier film, or onto an impermeable glass substrate.

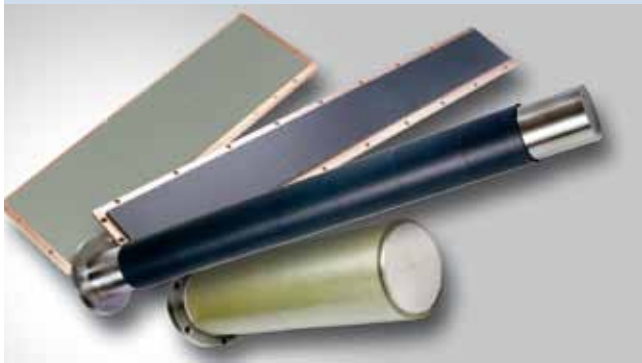
The Ca film is then sandwiched between the glass substrate and the test barrier and the edges of the sandwich are sealed using an edge seal material. The structure is considered semi-hermetic with respect to the test barrier's permeation so that the only avenue of water transport to the Ca film is through the barrier film. This entire assembly is put in a controlled environment chamber, where the amount of Ca oxide present (or alternatively, the amount of Ca missing) is detected by either optical [10] or electrical [11] schema.

Optical detection methods depend on the transition from opaque Ca to transparent Ca oxide. UV-Vis and ellipsometric measurements have both been used (in both reflective, as depicted, or transmission modes) to determine the amount of Ca oxide present. Spectra are taken at the start and then periodically throughout the test by which the amount of Ca degradation is determined from the change in transmission or the shift in the refractive index of the Ca layer. This corresponds to $Q(t)$ and can be used to obtain the WVTR (Equation 5).

The electronic detection method depends on the transition of the Ca film from a highly conductive metal to a non-conductive oxide. In this case non-corrosive (Au or Pt) contact pads are deposited onto the Ca film, so that the resistance of the film can be measured in either a two- or four-point configuration, and are then passed through the edge seal to the outside of the assembly. The amount of Ca remaining can be calculated from the resistance measurements (using an assumed bulk resistivity for Ca), and the WVTR can be calculated from the derivative of the change in conductance with time.

This test has good sensitivity ($10^{-6} \text{ g/m}^2/\text{day}$) and can monitor transients as well as steady state WVTR [10, 11]. Using different (or adjusting) environmental chambers, it is possible to have many different temperature and humidity conditions. High throughput is also possible, especially with the electrical detection methods. However, to the authors' knowledge there are no commercial systems available and no ASTM standards for the Ca test. Additionally, the equipment required for initial setup is expensive.

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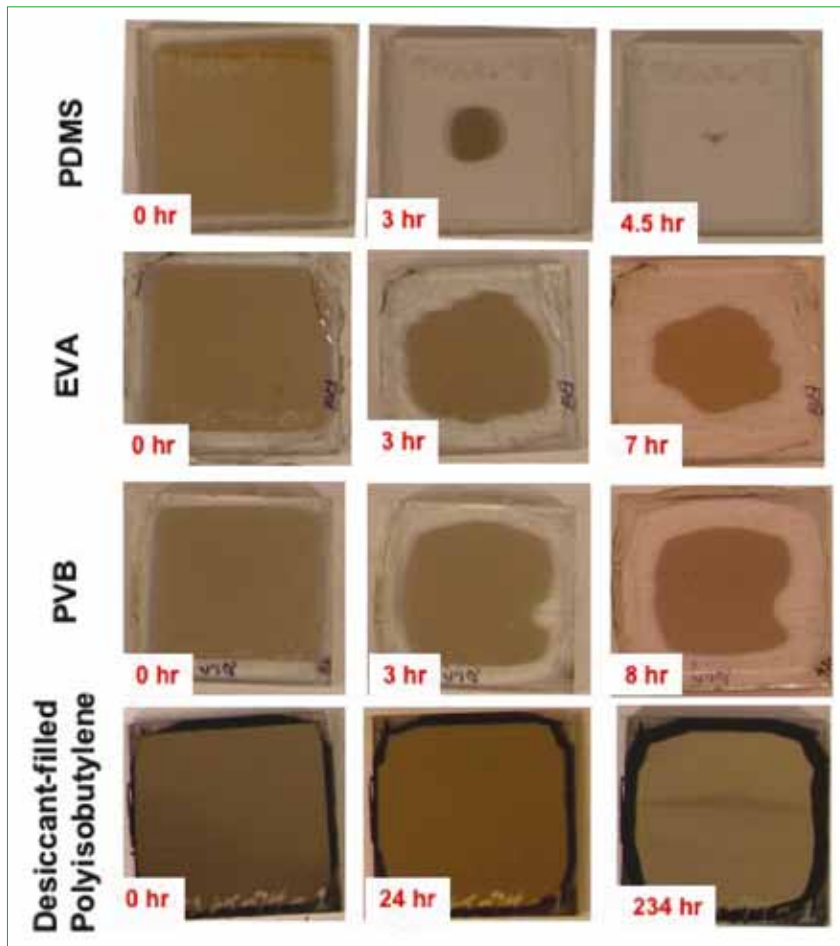


Figure 5. Photos of common encapsulant materials prior to environmental testing (0hr) and at demonstrative time points (indicated by time stamp), prior to complete degradation. Calcium's transition from opaque to transparent documents moisture ingress through the edges as illustrated in Figure 3.

Diffusion cell methods

Isostatic method

The dominant standard commercial instrumentation for WVTR measurements is the MOCON Permatron (ASTM-F1249). The MOCON instrument consists of a diffusion cell and an infrared sensor (see Fig 4C). From the gas stream on the measurement side of the barrier film, the infrared sensor measures the fraction of infrared light absorbed by the water, creating an electrical signal that is proportional in amplitude to the water concentration. The amplitude of the electrical sensor is compared to the amplitude of the signal from a calibration film with known WVTR properties to determine the actual WVTR of the test barrier. The more recently developed MOCON Aquatron uses a more sensitive coulometric detector that does not require a calibration standard.

The MOCON systems are some of the few commercially available WVTR instruments. More advanced models allow control over temperature and humidity, can measure up to six samples at once and can measure in real time to determine the breakthrough time as well as the steady state WVTR. However, the detection limits of the Permatron are $0.05\text{g}/\text{m}^2/$

day to $100\text{g}/\text{m}^2/\text{day}$ and the Aquatron limits are $5 \times 10^{-4}\text{g}/\text{m}^2/\text{day}$ to $5\text{g}/\text{m}^2/\text{day}$. Typically, systems are configured to only perform measurements on barriers up to 50°C without invalidating the warranty, although it is possible to configure them to test barriers up to 85°C using external test cells.

HTO/radioactive tracer method

The radioactive tracer method for measuring WVTR involves detection of water doped with tritium (HTO). Detection is done either directly using an ionization chamber [12] (Fig. 4D1) or indirectly by trapping any available HTO in a hygroscopic salt [13] (Fig. 4D2) and then measuring the tritium in the salt by scintillation methods. For both detection methods the water source side is a static HTO reservoir (RH100%).

In the case of the ionization chamber, a gas stream (usually methane) picks up any HTO that has penetrated the barrier film and carries it to the ionization chamber where the tritium is detected in real time. Using this method, the breakthrough time, lag time, and the steady state WVTR can be measured independently. The detection limits of the ionization chamber determine the limits of measurable WVTR, however, with adjustment of

the barrier test area these limits can be extended. Theoretical lower detection limits are $2.4 \times 10^{-7}\text{g}/\text{m}^2/\text{day}$ with practical detection limits $<1 \times 10^{-6}\text{g}/\text{m}^2/\text{day}$ [12].

“There are a variety of methods that have been developed to quantify water permeation. Each has limitations either in sensitivity, throughput, speed, or capital outlay/cost.”

In the case of the hygroscopic salt ‘detector’, a salt source (usually LiCl) that absorbs any available water (including HTO) is situated on the measurement side of the barrier. The salt is periodically exchanged for new salt and the amount of tritium in the salt is counted with scintillation methods. To determine the WVTR, the measured tritium is averaged over the time since the salt was changed. For this reason, the salt method is only accurate in the steady state regime (i.e., after breakthrough). The detection limits are a result of the limits of the scintillation counter. With adjustment of the barrier test area and adjustment of the time between salt exchanges, these limits can be extended. Reported detection limits are $\sim 1 \times 10^{-6}\text{g}/\text{m}^2/\text{day}$ to $3\text{g}/\text{m}^2/\text{day}$ [13].

Since the HTO test is most commonly set up with a static HTO source, the test is only run at 100 %RH. The temperature is adjusted by heating up the vessel containing the source, barrier and ‘detector’. It is also worth noting that, because the tritium is the detected species, this test method indirectly measures water. With the availability of a scintillation counter, the HTO test using the salt detection method can be set up quickly and inexpensively. Further, many samples can be run simultaneously. The ionizing detection method makes the initial setup more arduous, and is more difficult to multiplex. The major drawback of this method is the use of radioactive materials.

Mass spectrometry

Several methods for detection of WVTRs using mass spectrometry techniques have been reported [14,15]. For these measurements, UHV mass spectrometry techniques are used to measure the partial pressure of the water vapour permeating the barrier in a given integration time. This barrier bifurcates the UHV test chamber. While the upstream section of the chamber supplies metered water vapour, the mass spectrometer sits downstream to measure the WVTR. Both sections are evacuated (to $\sim 1 \times 10^{-8}$ Torr), then using a

calibrated leak valve a controlled partial pressure is introduced and monitored in the upstream section of the chamber. The pressure differential on each side of the test barrier is controlled to minimize the mechanical strain on the barrier. The partial pressure of the water that has diffused through the barrier is measured above the background in the downstream section of the chamber.

Mass spectrometry-type methods have reported the highest sensitivities for an integrated measurement termed programmed valving mass spectrometry (PVMS) (instrumental setup shown in Fig. 4E). For PVMS, the downstream section is separated into three sections by valves: accumulation area, measurement area, and pump. The accumulation area is between the test barrier and the first valve. The measurement area, which houses the mass spectrometer, sits between the accumulation and pump valves.

During the measurement, the accumulation area is open to the barrier and the accumulation valve is closed, while the pump evacuates the measurement area to establish a baseline reading on the mass spectrometer. After a given accumulation time the pump valve is closed and the accumulation valve is opened, resulting in a jump in measured partial pressure, which in turn corresponds to the integrated partial

pressure for the accumulation time. The whole downstream section of the chamber is then evacuated by opening the valve at the pump. This accumulate-measure-evacuate cycle is repeated; any measured change in partial pressure increases until a steady-state WVTR is established, thus the steady-state WVTR and the breakthrough time can both be measured. The reported lower detection limits for mass spectrometry WVTRs are $\sim 10^{-7} \text{g/m}^2/\text{day}$ [14]. The most beneficial aspect of this method is its ability to measure other gaseous species in addition to water, though sample throughput is a major drawback.

Moisture ingress comparison of commonly used materials

A test of the moisture ingress using calcium's transition from opaque to transparent when oxidized (see Ca Test section) was performed on several different materials commonly considered as encapsulants and edge seals in PV applications. The results of the test are shown in the photo array in Fig. 5.

To perform the test, 3mm x 5cm x 5cm glass was outgassed in a nitrogen glovebox environment with less than 1 ppm O_2 and H_2O . After outgassing the glass, 100nm-thick calcium films were deposited on half of the glass squares. Each material was outgassed in the inert

environment prior to assembly of the test structures. Overnight baking at 140°C was required to outgas the PIB edge seal material. The EVA and polydimethyl silicone (PDMS) were heated at 60°C while the PVB was heated at 100°C. Without sufficient outgassing, residual moisture in the encapsulants/edge seal materials rapidly degrade calcium. In assembling each structure, a heated mechanical press was used to evenly apply pressure to all structures except the silicone samples. A uniform separation of the glass squares was achieved by using a 0.25mm-thick release liner as a spacer. After assembly, samples were left in the glovebox overnight to ensure that all recorded calcium degradation was a result of ingress rather than interaction with the encapsulants.

Thin Film

“The breakthrough time does not depend on the solubility for a Fickian material and is thus a qualitative measurement of the diffusivity or the effective diffusivity for non-Fickian materials.”



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After baseline measurements were made of each sample area and photographs were taken, the samples were stored in an 85°C/85% RH environmental chamber and periodically removed for monitoring. Time in Fig. 5 refers to the time spent in the environmental chamber, although effort was taken to minimize time in ambient conditions. It is worth noting that the environmental chamber takes approximately 5-10 minutes to stabilize after being opened.

The test illustrates the radically different rates of moisture ingress as the encapsulant is varied. The rate of ingress as determined by this test is essentially monitoring the breakthrough time for a very low percent of the steady state value. The percent of steady state WVTR necessary to produce the breakthrough profiles in Fig. 5 will vary from material to material, but this should not have a significant effect on the constant used in Equation 8. Therefore, as shown in Equation 7, the breakthrough time does not depend on the solubility for a Fickian material and is thus a qualitative measurement of the diffusivity or the effective diffusivity for non-Fickian materials. Thus, a method for comparison of the diffusivity (or effective diffusivity) of candidate edge seal materials has been established.

Conclusions

With careful consideration of encapsulant and edge seal materials and insightful packaging strategies, current PV technologies can withstand environmental conditions for the required 20 years. However, more research is required to develop materials for the more demanding and sensitive flexible and thin-film technologies. Many more reliability studies are required to measure and fully understand the diffusion properties of newly developed materials. While this paper has covered some of the underlying physics of moisture ingress as well as general packaging strategies including some of the principles and material properties that should be considered in module designs, putting them into practice effectively requires that attention is paid to several more details. These include ultraviolet (UV) stability, good adhesion/delamination, uniform assembly (i.e. control of edge pinch or flare), and mechanical stress. While a complete understanding of the effects of a single stress such as moisture, UV exposure, heat, or physical strain is always useful for continued improvement of particular materials, thorough knowledge of how coupled stresses affect a system is required for effective and reliable packaging.

Acknowledgements

The authors acknowledge funding received from DOE contract #DE AC 36-99G010337.

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