

Water Vapor Permeation Testing of Ultra-Barriers: Limitations of Current Methods and Advancements Resulting in Increased Sensitivity

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ABSTRACT

Advancements in barrier quality of certain materials have pushed the sensitivity limits of commercially available water vapor permeation equipment. In order for products such as OLED's which incorporate these high barrier materials, to be viable, current permeation testing methods must be enhanced or altered. In designing a more sensitive method, the limitations of the current methods were first studied. From there, enhancements and modifications to the traditional comparative or concentration sensor produced an order of magnitude increase in sensitivity (from 5×10^{-3} to 5×10^{-4} g/m²/day.) Permeation results illustrating the new system will be presented as the highlight of the paper. Limitations found in the current methods, alterations made to a traditional system and insight into future modifications that will increase the sensitivity even further will also be included.

INTRODUCTION

A major hurdle for the introduction of flexible OLED's into the commercial market is the limited lifetime of the devices due primarily to the degradation in the presence of moisture and oxygen. Permeation barriers are required to minimize the exposure of the devices to the moisture and oxygen in the atmosphere. A water vapor transmission rate (WVTR) value of 1×10^{-6} g/m²/day has become the unofficial standard for the OLED industry to achieve a device lifetime of >10,000 hours. This value was originally estimated by calculating the amount of oxygen and water needed to degrade the reactive cathode. Obviously an impediment is the development of these barrier materials, however, a concurrent problem is a WVTR method to measure these materials as they are developed.

CURRENT WVTR TESTING METHODS

ASTM F1249

A long-time standard used in a variety of industries to measure the WVTR through flexible barrier materials. In this method, "a dry chamber is separated from a wet chamber of known temperature and humidity by the barrier material to be tested. The dry chamber and the wet chamber make up a diffusion cell in which the test film is sealed. Water vapor diffusing through the film mixes with the gas in the dry chamber and is carried to a pressure-modulated infrared sensor. This sensor measures the

fraction of infrared energy absorbed by the water vapor and produces an electrical signal, the amplitude of which is proportional to water vapor concentration. The amplitude of the electrical signal produced by the test film is then compared to the signal produced by measurement of a calibration film of known water vapor transmission rate. This information is then used to calculate the rate at which moisture is transmitted through the material being tested." (ASTM F1249)

Calcium Test

Also known as the Ca Button Test, this method is based on the corrosion of thin calcium films. It involves observation of the optical changes as Ca converts to a transparent calcium salt as water vapor permeates through the barrier material. Because a visual change is observed, the Ca test can distinguish between bulk permeation and defect-based permeation, however it does not discriminate between oxygen and water permeation.

Radioactive Method

This permeation method, based on the same general concept of ASTM F1249, uses tritiated water as the permeant and a device to measure radioactivity.

Modified ASTM 1249 (modified detector)

Using the same protocol as ASTM 1249, this instrument, the MOCON AQUATRAN, utilizes a coulometric detector to measure the water vapor permeate. The addition of the absolute coulometric sensor increases the sensitivity by an order of magnitude over the traditional ASTM 1249.

HURDLES IN MEASURING PERMEATION

Regardless of the method used, several obstacles are inherent to permeation testing. Without proper measurement and/or control of the variables, permeation results can vary drastically. Because of these obstacles, low-end results from all current methods should be closely examined.

Temperature

Permeability is a function of temperature. The Arrhenius equation, $P = P_0 * e^{(-E/RT)}$, where P is the permeability, P_0 is the permeability constant, E is the activation energy, R is the gas constant, and T is the temperature, relates temperature to permeability. As a general rule of thumb a

one degree (centigrade) change in temperature results in a ten percent change in permeability. Therefore, precise temperature control is crucial to reliable, accurate permeability measurements. In a typical laboratory, the temperature can fluctuate up to four degrees centigrade in a twenty-four hour cycle. Without proper control of temperature in the permeability experiment, results can vary by upwards of forty percent.

Leaks

Leaks present a major hurdle when measuring permeability of water vapor because of the moisture in ambient air. Regardless of the method or sensor used, it is imperative to account for only the moisture due to the flux, not from an ambient leak. A seemingly small leak of 1 ppm water vapor results in a permeation rate of 0.01 g/(m²-day.) Also, because the amount of moisture in ambient air is continually changing, there is no fixed background or leak value that can be subtracted to obtain a reliable permeation answer.

In the case of the calcium test, the inability to distinguish between oxygen and water vapor poses a similar problem.

Calibration

Most sensors are comparative or concentration-based and require calibration. They operate on the notion that an electrical signal is produced based on the reaction of the sensor. A calibration is needed to produce an electrical signal response curve. This curve is then used for subsequent unknown runs where the amount of compound is interpolated from the resulting signal. Additionally, these sensors typically measure only a fraction or ratio. It is important that sensors be calibrated in the range which they are used. If calibrating to an actual amount of water, the lowest NIST traceable calibration gas is 10 ppm +/- 10%. This corresponds to a water vapor transmission rate (WVTR) of 0.1 g/(m²-day). The desired goal of the OLED industry is a transmission rate of 1 x 10⁻⁶ g/(m²-day), this corresponds to a calibration level of 0.0001 ppm (0.1 ppb) of water vapor. Factors that play a role in typical permeation such as temperature, flow control and repeatability, are only compounded by calibration.

System Noise

System noise encompasses a variety of variables and serves as a sort of catch-all for anything not listed above. Examples of system noise in permeation measurement related devices include electronics, system outgassing and carrier gas variability.

Almost all sensors have some noise associated with electronics. The goal is to not only minimize the noise but to measure and adjust final values to account for it. System outgassing includes the absorption and desorption of moisture from any system components beyond the test sample in the gas sensing path including valves, o-rings and lines. Finally, similar with leaks, the carrier gas must

be completely void of any moisture prior to contacting the test sample.

Correlation to Established Methods/Results

When test results can be correlated to results obtained from an established albeit cumbersome method, additional validation is provided. A chilled mirror or hygrometer provides an excellent validation method for barriers in the 0.01 g/(m²-day) and above ranges. Although the hygrometer is not optimal for everyday testing, it provides a basis for comparison of others methods. A major impediment in the advancement of barrier measurement technology to 1 x 10⁻⁶ g/(m²-day) is the distinct lack of this type of correlation technology – there is no “stake in the ground” to compare results.

ADVANCEMENTS IN PERMEATION MEASUREMENT TECHNOLOGY

MOCON AQUATRAN – Modified ASTM F1249

Replacing the concentration-based pulse modulated infrared sensor with an absolute coulometric sensor increased the sensitivity of MOCON AQUATRAN® by an order of magnitude. Although this instrument does not yet reach the 1 x 10⁻⁶ g/(m²-day) goal, it provides accurate, reliable permeation results to 5 x 10⁻⁴. Listed below are the modifications and enhancements according

Temperature

As with MOCON's Permatran-W® Model 3/31, a long-time standard in the permeation measurement industry, the AQUATRAN has excellent temperature control. The temperature of the test sample is maintained within one tenth of a degree centigrade of the setpoint, thus eliminating any temperature related errors.

Leaks

Minor modifications have been made to the AQUATRAN to counter the issue of leaks. This is an area for future improvement in sensitivity.

Calibration

The AQUATRAN contains a coulometric sensor. This sensor is absolute or intrinsic. It measures the total amount of the sample versus only a fraction like a concentration based sensor and, most importantly does not require calibration. Because no calibration is required, many of the measurement hurdles have been overcome. The sensor is more accurate over the full range and coulometric technology is not affected by pressure, temperature, flow or vibration. The potential sensitivity of the sensor itself is 2 x 10⁻⁶ g/(m²-day.)

A coulometric sensor measures the electricity required to carry out a chemical reaction. The reactions are carried

out at the electrodes and the reaction must proceed to the maximum allowed by Faraday's Law, which means it is near 100% efficient.

System Noise

Changing the sensor actually reduced the system noise by eliminating some noise associated with the electronics. Additional work can still be completed to improve system outgassing and carrier gas technology, thus further improving sensitivity.

Correlation to Established Methods/Results

Although there is still no "stake in the ground" at 5×10^{-4} g/(m²-day), results from the AQUATRAN have been correlated to a chilled mirror, gravimetric measurements and the MOCON PERMATRAN-W 3/31 at the low range. The AQUATRAN has also exhibited excellent linearity, indicating accurate, reliable results at its low range.

Data / results

Many barrier samples have been tested on the AQUATRAN. Table 1 lists some sample results obtained. Note that package configurations can also be tested. The WVTR units for packages are mg/(package-day). Also note mass units have been changed to mg due to small measurement values.

Table 1. AQUATRAN WVTR Data.

SAMPLE	WVTR (mg/m ² -day)
A	77.0
B	85.0
C	46.7
D	<0.5
E	<0.5
F	0.071 mg/pkg/day
G	<0.003 mg/pkg/day

CONCLUSION

As barrier quality continues to increase, so too must permeation testing methods. Several hurdles exist when measuring permeation including temperature control, leaks, calibration and system noise. Most existing testing methods are deficient in most of these areas, thus producing unreliable results in the low range of sensitivity. The AQUATRAN eliminates calibration with the addition of an absolute sensor and increases sensitivity by an order of magnitude. Proven WVTR values to 5×10^{-4} g/(m²-day) are reliable and accurate. Although the sensitivity has not yet reached the desired 1×10^{-6} g/(m²-day), the new sensor has the capability of reaching that goal. The remaining hurdles have been

identified to bring the entire system to that level. Currently, even a $<5 \times 10^{-4}$ g/(m²-day) result obtained from the AQUATRAN is an extremely valuable piece of information because of the accuracy and repeatability that are inherent in this method and may not be in others.