

A new method for measuring ultra-low water vapor permeation for OLED displays

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Abstract

It is well known that proper encapsulation is crucial for the lifetime of organic light emitting diode (OLED) displays. With the development of increasingly better barrier coatings and perimeter seals, it has now become very desirable to be able to precisely measure the rate of water vapor and oxygen permeation through barrier coatings and perimeter sealing. This paper demonstrates a new permeation measurement method that uses tritium-containing water (HTO) as a tracer material. The theoretical detection limit of this direct method is 2.4×10^{-8} g/(m²·day).

1. Introduction

Flexible OLED displays have the potential to become the next generation of flat panel displays. They carry the advantages of being rugged and conformal, requiring low power consumption and superior viewing capability and may offer lower cost due to roll-to-roll manufacturing. However, the materials currently used in OLED displays are very sensitive to moisture and oxygen. The reaction of the emitter and cathode materials with water and oxygen results in severe device degradation. A permeation rate of water vapor $< 10^{-6}$ g/m²·day is reported to be required for OLEDs¹. However, plastic substrates do not show intrinsically high barrier performance. Many efforts have been made to develop high quality barrier coatings on plastic substrates. Coatings with a single inorganic layer or stacks of alternating inorganic/organic layers have been reported to significantly reduce the permeation rate². As barrier coatings have improved in their resistance to moisture and oxygen permeation, it has become clear that more accurate methods and apparatuses are required to measure increasingly lower rates of permeation.

The most commonly used tools for measuring water vapor and oxygen permeation through plastic films are instruments made for food packaging by

MOCON, Inc. Their current detection limit is approximately 0.005 g/(m²·day) for water³. There are many permeation-testing methods that have been developed recently. These methods use detection principles that are gravimetric, capacitive or resistive, spectroscopic, or based on calcium degradation^{4,5}. Here, we present a permeation measurement method and apparatus for measuring ultra-low water permeation. This method uses tritium-enriched water (HTO) as a tracer material⁶. The apparatus can be used to measure the permeability of polymer substrates with barrier coatings as well as the permeability of perimeter sealing for OLED displays.

2. Experimental

2.1 Setup

The system consists of a gas supply system, a test chamber that holds the sample and the tracer material, and an ionization chamber with a counter and a recording device. The experimental schematic is shown in Fig. 1. A 100 x 100 millimeter sample is placed into the test chamber and mounted between two square O-rings on each side. Outside of that, a round O-ring seals the test chamber. Due to the setup of the chamber, the effective sample size for plastic samples is 86.5cm².

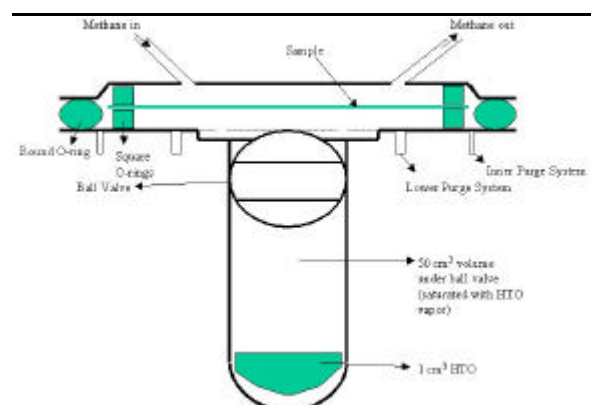


Fig. 1 Cross-section of the radioactive tracer test.

A Teflon coated ball valve separates the reservoir

containing the tracer material from the sample. To accelerate the experiments, the entire assembly is equipped with multiple thermocouple controlled heating elements. This enables control of both the sample temperature and the relative humidity. Although smaller or higher quantities could be used, for our current experiments the reservoir was loaded with 1 cm^3 of tritiated water (HTO) with a specific radioactivity of 1 Ci/cm^3 . This HTO loading concentration can provide a radioactive source for as long as one year under normal test conditions and usage. Since tritium is not the only beta-emitter, natural radioactivity or cosmic rays may also have an impact on the measurement, and a baseline needs to be recorded for 8-12 hours. Once the sample is placed into the tester and a stable baseline is obtained, the ball valve is opened. During the test, tritium containing water vapor permeates through the sample and is picked up by a dry methane stream with a flow rate of 1 liter/hour and fed into an ionization chamber for instant radioactivity measurement. The ionization chamber (Femto-Tech 224RM-U24-D) is a calibrated device that records the ionization of beta decays in μCi per cubic meter; it has a volume of 1.8 liters. High measurement sensitivity can be achieved by using only a very slow flow of dry gas as a carrier and by minimizing the size of the test chambers and the monitoring chamber.

2.2 Physical Fundamentals and Calibration

For 1 cm^3 of volume and a specific radioactivity of 1 Ci/cm^3 , the tritiated water is a mixture of molecules of HTO and H_2O where every $1/1,667^{\text{th}}$ molecule is HTO. The diffusion behavior of HTO and H_2O is very similar; the difference can be calculated with the square root of their molecular weights (see equation [2]). At any given temperature, the air over the HTO becomes saturated with HTO and H_2O vapor to represent 100% relative humidity condition under the sample. By controlling the temperature of the reservoir independently from the temperature of the sample, it is possible to establish a range of relative humidities relative to the sample temperature. The gap under the sample is designed to be very small (0.04 inches) to ensure quick equilibration. We have modeled the time it would take for the volume under the sample to become saturated with HTO/ H_2O vapor and have calculated approximately 5 minutes. The response curve after the ball valve is opened is shown in Fig. 2.

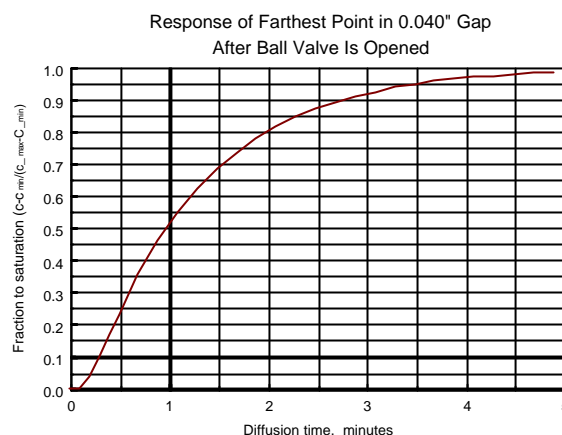


Fig. 2 Calculated water vapor equilibrium curve after the ball valve is opened.

Methane was chosen because it has a similar molecular weight to water and also has a favorable ionization rate. The theoretical detection limit can be calculated taking into account the ionization rate of methane, the half time of tritium (only 5% decays in the first year, see Figure 3), the difference in diffusion of HTO and H_2O and converting the radioactivity counts per cubic meter with the flow rate of methane into counts per 24 hours and relate it to 1 square meter of area.

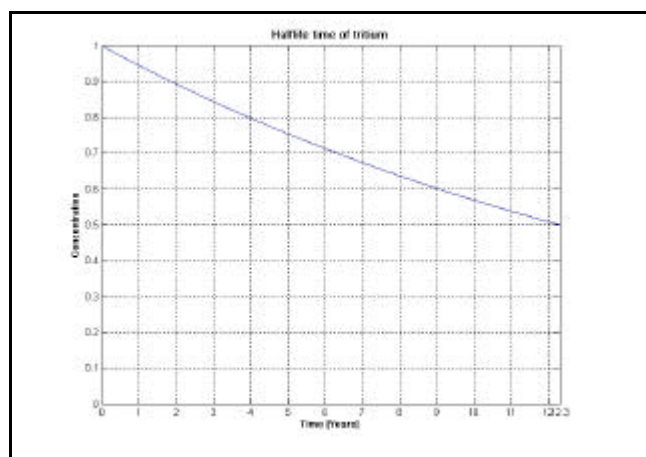


Fig. 3 Decay curve of tritium.

The methane mass flow controller is set to a constant flow rate of $16.67\text{ [sccm of CH}_4\text{]}$.

$$[1] \quad \text{Flow} \left[\frac{m^3}{\text{day}} \right] = \frac{\text{Flowmeter Reading} \cdot 60 \cdot 24}{10^6}$$

[2]

$$\text{WaterAmount}[g] = 1Ci \cdot \sqrt{\frac{M(\text{HTO})}{M(\text{H}_2\text{O})}} \cdot e^{y \cdot \frac{\ln 0.5}{12.5}} = 1.054 \cdot Ci \cdot e^{y \cdot \frac{\ln 0.5}{12.5}}$$

The first term in equation [2] describes the variation of water permeation due to different molecular weight of HTO and H₂O, while the second term describes the radioactive decay of tritium (Y=Years, halftime 12.5 years). Since the ionization chamber was calibrated in

air the reading in $\left[\frac{Ci}{m^3} \right]$ must be divided by a factor of

1.25 since the ionization factors are different between air (33.8) and CH₄ (27.3).

[3]

$$\text{PermRate} \left[\frac{g}{m^2 \cdot \text{day}} \right] = \frac{(\text{Value} - \text{Baseline})}{1.25 \cdot \text{SampleSize}} \cdot \text{Flow} \cdot \text{Water Amount}$$

The permeation rate of barrier coated plastic samples is obtained using equation [3]. The permeation rate of perimeter sealed glass samples is calculated with formula [4].

[4]

$$\text{PermRateGlue} \left[\frac{g}{\text{day}} \right] = \frac{(\text{Value} - \text{Baseline})}{1.25} \cdot \text{Flow} \cdot \text{Water Amount}$$

Using equation [3], the theoretical detection limit for barrier-coated plastics can be calculated (equation [5]). The resolution of the counter that is attached to the ionization chamber is 0.1 μCi/m³. Tritiated water is available with a specific activity of 10 Ci/cm³ where 1 Ci equals 1/10 gram of water. The maximum plastic sample size is 86.5cm². Thus, the theoretical detection limit is 2.4 x 10⁻⁸ g/(m²·day).

[5]

$$\text{MinWVTR} \left[\frac{g}{m^2 \cdot \text{day}} \right] = \frac{(0.2 - 0.1) \cdot 10^{-6}}{1.25 \cdot 0.00865} \cdot \frac{16.67 \cdot 60 \cdot 24}{10^6} \cdot \frac{1}{10} \cdot 1.054 = 2.4 \cdot 10^{-8}$$

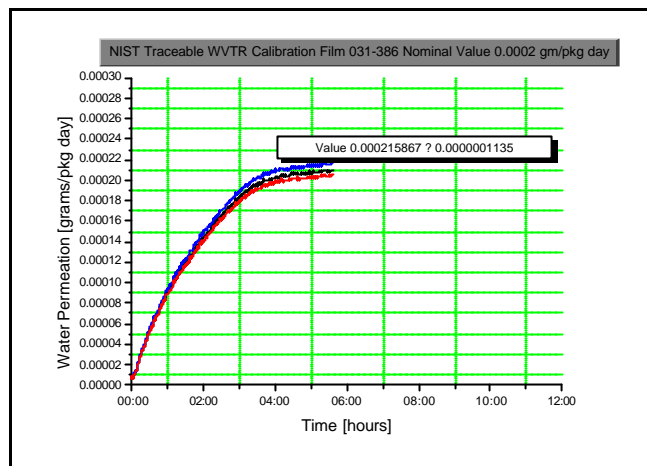


Fig. 4 Validation of method with NIST traceable standard..

We have validated our testing method with a NIST traceable water vapor standard. The result of three repeated measurements is shown in Fig. 4.

By using radioactive ¹⁴CO, instead of HTO, the test can be potentially carried out to measure oxygen permeation. ¹⁴CO is also a beta-particle emitter. The size of the oxygen (O₂) molecule is very close to the size of the carbon monoxide (CO) molecule. The CO molecule is slightly more polar but the molecular weights are quite close. Therefore it has been determined that the use of carbon monoxide can provide a very close approximation to O₂ permeation, but future work includes calibration with a NIST traceable standard to validate this method. The carrier gas may be oxygen instead of methane.

2.3 Permeation measurement for coated polymer films

A polymer film with a typical thickness of 0.125 mm is directly mounted in the central receptacle. In most cases it is mounted with the barrier-coated side facing down (in direct contact with the water vapor) but occasionally we obtain samples that have a barrier coating on both sides. The orientation does not seem to matter, the only difference we observe is the lag time. 99.99% pure methane is used as a carrier gas for water vapor permeability measurements. Once the apparatus is closed, first argon and then methane is sent through to purge the volume below the sample. Following a similar purging of the upstream chamber, the ball valve is opened, causing HTO vapor from the underlying reservoir to flow into the upstream

chamber. Typically the film saturates fairly rapidly with HTO/H₂O vapor and a uniform methane flow is passed through the upper chamber at a rate of 16.67 sccm - and run through the ionization chamber. After a certain lag time, a breakthrough occurs and HTO is detected in the ionization chamber. Given the fairly high diffusion coefficients of polymeric materials such as Polyethylene Terephthalate (PET) or Polycarbonate (PC), the lag time is mostly driven by the diffusion coefficient of the inorganic barrier material⁷. Depending on the temperature, the quality of the coating and the number of layers, the test may take between 24 and 300 hours to reach steady state. When the test has been completed, the ball valve is closed, and the upstream and downstream subchambers are sequentially purged until the monitor is detecting no radiation.

2.4 Permeation measurement for perimeter seal

Glass plates have long been used as protection for OLEDs due to their excellent resistance to both oxygen and moisture permeation. To bond both glass plates together a perimeter seal is typically applied. However, since organic materials (e.g. UV cured epoxies) are often used as perimeter seal, a desiccant is added to the display architecture to capture the moisture and oxygen that enters from the lateral direction into the packaged device. As a result, it has become important to be able to determine the effectiveness of the perimeter seal. An arrangement for testing perimeter sealing using the radioactive tracer method is shown in Fig. 5. A large hole is created centrally within a 1.0 mm thick glass plate that has essentially the same dimensions as the standard film samples (100 mm x 100 mm). A round thin glass disk with a diameter larger than the hole is placed on top. With a liquid dispenser a continuous and uniform line of edge sealant is accommodated between the glass disk and the plate around the hole. The thickness and the width of the seal can be varied but are typically chosen to represent manufacturing conditions. The assembly of the plate and disk is mounted in the central receptacle. When the ball valve is opened, the HTO vapor will pass through the large hole and will eventually permeate through the perimeter seal, where it will then enter the downstream subchamber. Thus, the apparatus is also useful for testing the barrier properties of an edge seal in an accurate manner.

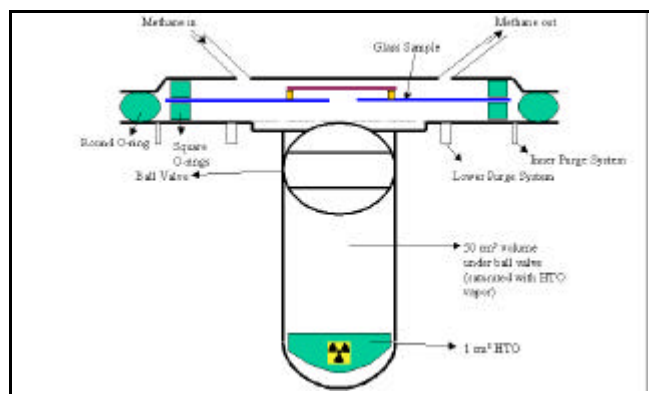


Fig. 5 Arrangement for testing perimeter sealing.

3. Results and discussion

3.1 Permeation measurement of barrier coated plastics

We have tested single layer barrier coatings on PET (Melinex ST 505) and PC (Lexan High T_g). The AlO_x barrier layer on PET was deposited in our lab using pulsed DC magnetron sputtering. The Lexan sample with a PECVD deposited layer of silicon oxynitride was obtained from General Electric. The permeation curves are displayed in Fig. 6 (blue curve is PET, black curve is PC).

The abscissa indicates the test time after the ball valve is opened. The ordinate indicates the calculated water permeability and is plotted logarithmically. The tests were carried out at room temperature (approximately 23°C) and 100% RH. Both experimental curves can be divided into two regions. During the first hours, the permeation increases rapidly. After about 60 hours, the permeation rates start to reach steady state. The slight waves in the curve can be attributed to slight temperature changes in the room due to day and night. The data set shows a considerable noise level below permeation rates of $\sim 1 \times 10^{-6}$ g/(m²-day).

3.2 Permeation measurement of epoxy materials on glass

UV-cured epoxy bonding materials were obtained from Masterbond (UV16). To study repeatability of our testing method with identical thicknesses and bond widths, we prepared to the best of our abilities two identical samples with a bond width of 2.5 mm and a bond thickness of approximately 50 microns.

Both tests were carried out at 38°C and 100% RH.

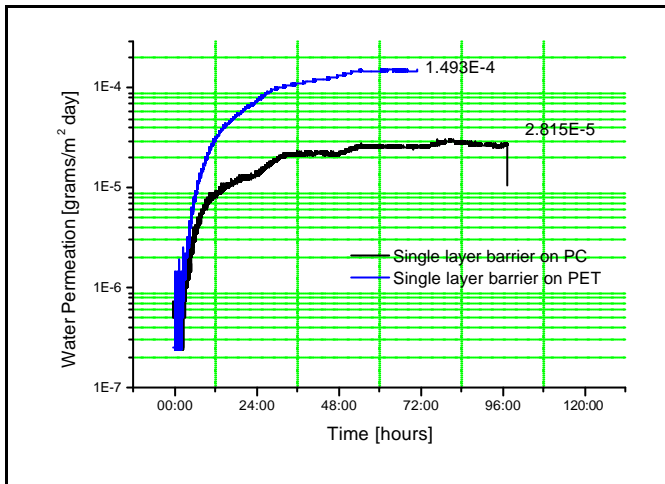


Fig. 6 Permeation curves for a PET and PC film coated with a single barrier layer.

The results of these two permeation experiments for epoxy edge sealing materials on glass are plotted in Fig. 7. The black curve represents the first sample measurement, the red curve the second sample measurement. The blue lines are curve fits using Microcal Origin's sigmoidal curve fit function with the parameters printed in the boxes. At 400 hours, the extrapolated water vapor permeation is 1.287×10^{-4} grams/day and 1.188×10^{-4} grams/day, indicating that both measurements differ by 8.3%.

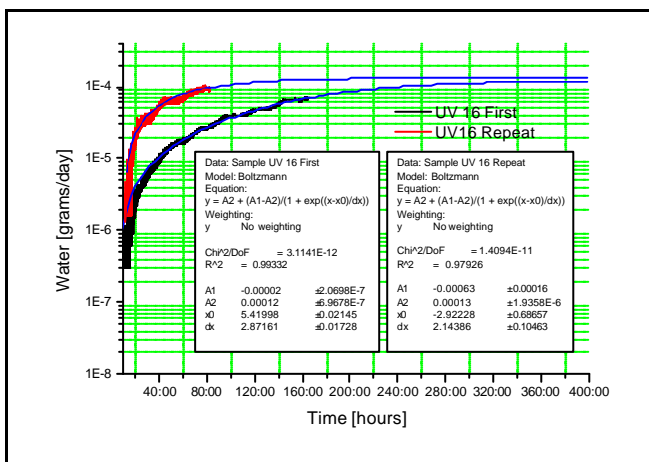


Fig. 7 Permeation curves for epoxy edge seals on glass with different bond widths.

4. Conclusion

A new method for testing ultra-low moisture permeation by using HTO as a tracer material has been established. High measurement sensitivity can be achieved by using only a very slow flow of dry gas as a carrier and by minimizing the size of the test chambers and the monitoring chamber. The test method has been applied to test the barrier performance of single layer coatings on plastic as well as the leak rate through epoxy materials on glass. Contrary to the calcium test, this method provides the absolute number for water vapor permeation, both instantaneous and in steady state. The theoretical detection limit of this direct method is 2.4×10^{-8} g/(m²·day).

5. Acknowledgements

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6. References

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