Measurement of WVTR through ultra barriers

Background

The need for measuring the throughput of water vapour through packaging films or barriers has numerous drivers. The obvious one of typical food packaging is now well served by readily available permeation measuring instruments. The more demanding requirement for films used for the present commercial generation photo voltaic solar cells is arguably within the limit of present day commercial instruments. However the need for extreme hermeticity to water vapour in the construction of organic LED displays has set the latest challenge to the instrument manufacturers. Reputedly a water vapour transmission rate (WVTR) of less than 10^{-5} g/m^2/day will endow OLED displays with a lifetime of better than 1 year[1] after which time the internal electrodes will be increasingly compromised. Barrier manufacturers are now looking towards WVTR performance of 10^{-7} g/m^2/day, to provide commercial products with more useful lifetimes. These materials can only be currently produced in multi-layered form, alternating traditional organic polymer film with inorganic metallic materials. In this way, despite defects in the individual layers, labyrinthine paths[2] are created to hold back gas and vapour throughput.

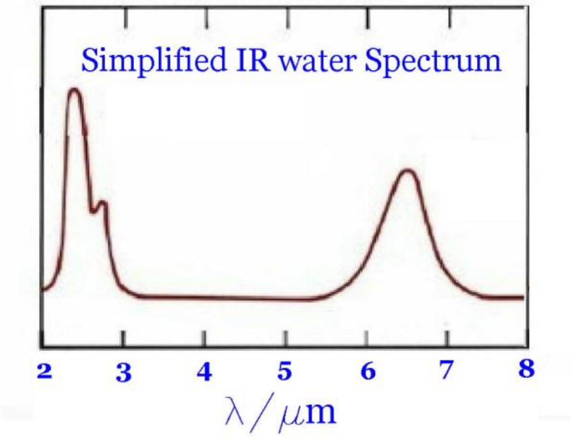
Techniques for measurement

Traditionally a system to measure WVTR comprises a wet and adjacent dry chamber separated by a sheet of barrier material under test. Strict control of the wet and dry environments, combined with moisture measurements can, using Fick’s Law, be used to calculate the water transmission through the barrier. The law simply states that diffusion through a barrier is a linear function of the concentration gradient across the barrier and its thickness. So with knowledge of the water vapour concentration on both sides, and the dimensions of the barrier, WVTR can be found. So the task becomes one of measuring the moisture levels on both sides of the barrier under test. To put this in perspective the 10^{-5} g/m^2/day WVTR mentioned above with respect to OLEDs, is the equivalent of less than 0.2 ppbv water vapour content in the dry chamber of a typical permeation instrument configuration.

There are a number of candidate sensing methods for moisture measurement, and the low moisture dry chamber trace level task will be considered exclusively. The most common techniques for trace water are infra-red (IR) light spectral absorption, mass spectrometry, metallic Calcium oxidation rate and Coulometric electrochemical cells. Of these the IR techniques can be further divided into four readily identifiable contenders, Fourier transform IR, cavity ring down spectroscopy (CRDS), tuneable laser diode (TLD), and non-dispersive or filtered IR.

FTIR, based on multiple peak identification in the spectrum, has long been the research grade technique of choice, but is not a leader in the commercial arena, being complex and expensive. CRDS is based on the concept of measuring the decay time of a very short laser pulse fired into resonant cavity containing the gas to be measured. The IR pulse spectrally selected for water will decay slower with less water present. It has a performance close to the present requirement for film WVTR testing and indeed has been used in this capacity[3]. This study at the NPL, UK appears to be a proof of concept, and it’s likely a commercial implementation would be expensive with no clear path for measurement enhancement.

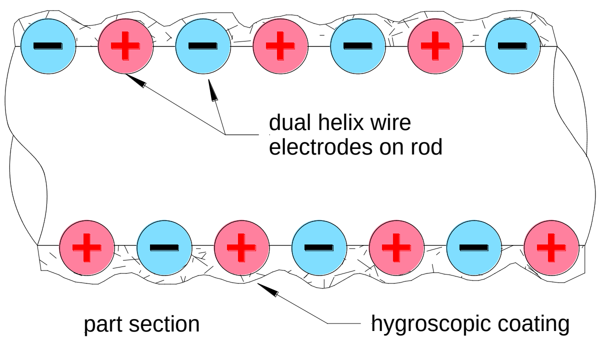
TLD spectroscopy, with the potential for very narrow bandwidth, has seen a lot of work over the last decade, and may be suitable for future permeation measurement. NDIR, usually based on the absorption of a single optically filtered peak, is well established in permeation instrumentation from a number of suppliers. However commercial instruments have a limit of detection orders of magnitude above the present requirements for barrier performance.



Mass spectrometry is capable of measuring almost any gas species with its ability to detect the molecular weight of ions within its detector. It does however need to operate at low vacuum pressures, and therefore to cope with near atmospheric pressures a sophisticated gas sampling system has to be employed. This, together with its complexity and costs have thus far restrained its use to academic research.

Calcium thin films are converted to the hydroxide in the presence of moisture, which conveniently has very different optical and electrical properties to the metal. Initially appearing to be a crude technique, research using both changes in resistance and optical transmission, show it can approach the required sensitivity for testing the latest barriers. Additionally the often mentioned interference by Oxygen, also reacting with the Ca, has recently been shown to be insignificant[4]. That said, it has only been used for one off experimental measurements in laboratory conditions and does not easily lend itself to instrument design. One of its problems being a very limited dynamic range, restricted to the lowest permeation range.

Typical Coulometric moisture sensor



Finally Coulometric sensors, based on the electrolysis current of the water vapour absorbed in a hygroscopic material, are the technology of choice for various permeation instrument makers. Systech Illinois Instruments have been at the forefront in the development of these sensors for a number of years, which provide an economical yet potentially extremely sensitive solution.

Calibration and Standards

Most of the IR absorption instruments have a characteristic response to water vapour concentration which is a function of the instrument detector design, and can be subject to drift over time. Consequently they need calibration from time to time. By contrast Coulometric sensors are subject to Faraday's Law which relates the electrochemical dissociation of a water molecule to precisely 2 electrons, therefore providing a current which is absolutely related to the amount of water consumed. To an extent Calcium conversion techniques may also claim to have absolute calibration when the stoichiometry of the chemical reaction is considered, providing all the water is consumed.

Standards for calibration are available in the form of traceable gas bottles. Once again the NPL have been active in this area[5], with the ability to produce standards over the range 5-2000 ppbv; undoubtedly alternative sources are available. A further standard is a calibrated barrier of some sort provided by the instrument manufacturer, itself calibrated in turn from a traceable standard.

In addition to the moisture metrology aspect the methodology of the barrier characterisation must be carefully considered to avoid the downfalls of leaks, traps, contaminant gases etc. To this end a several national standards have been drawn up to define broad rules for instrument design and operation, two for example are ASTM F-1249 for modulated NDIR instruments and ISO 15106-3 for electrolytic (Coulometric).

Comparison of commercial instrumentation

There are two classes of commercial permeation measurement instruments commonly available. These are the NDIR spectroscopic absorption designs and the Coulometric instruments.

NDIR instruments offer convenient, ease of use measurements with low maintenance, and relative ease of use. Some can also offer the dual roles of Oxygen transmission rate and WVTR. These permeation measurements are not absolute, so periodic calibration against a standard will be necessary to combat any drift and maintain accuracy. The current NDIR offerings appear to have now reached their limit of detection, at about 10^{-3} $g/m^2/day$, with no likely prospect of increasing sensitivity.

Coulometric WVTR measurement usually requires a little more housekeeping in the form of sensor maintenance, but beyond that modern digital instruments are straightforward and user friendly. They also have the great benefit that the measurements are absolute, therefore directly related to the precise amount of water vapour transmitted, and do not require the use of a standard. The latest instruments have already exceeded the sensitivity of the NDIR types with further improvements within reach. Systech Illinois Instruments, remaining mindful of wider developments, have specialised in this type of permeation measurement, and with their bypass sensing design can provide a linear response over full range. Operating a policy of continuous development of their in house sensors and instruments, they have the needs of the OLED community firmly within their sights.

Footnotes

1 S. Schubert, H. Klumbies, L. Müller-Meskamp, and K. Leo, Rev. Sci. Instrum. 82, 094101 (2011)

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