Evaluation of gas permeation through barrier layers for organic electronic devices by helium detector method

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Evaluation of gas permeation properties through barrier layers is important for the development of flexible organic light-emitting devices (FOLEDs). In this reported work, an helium (He) leak detector was used in a novel permeation test for metallic barrier layers. Aluminium (Al) or chromium (Cr) film was deposited as a barrier layer onto a polyethylene terephthalate (PET) substrate using a magnetron sputtering system. For the samples of PET substrates with Al and Cr films at thicknesses of 200 nm, the He pressures were 3.1×10^{-6} and 1.3×10^{-5} Torr, respectively, as measured via He detector testing. The poor permeation blocking by the Cr film was because of microcracks. The He pressure for samples with 1 000 nm thick Al coating and for Al foil (30 µm) showed different values of 3.2×10^{-8} and 1.1×10^{-10} Torr, respectively, which indicated high sensitivity in a low permeation range. The high sensitivity in permeation properties measured by He detector testing reflected the qualities of He that include one of the lightest weights known to science and a very small size. This He detector test will be useful in the development of long-life FOLEDs, as it will aid the measuring of the gas permeation properties of barrier layers that are highly effective in blocking water vapour.

1. Introduction: A challenging issue in the maintenance of flexible organic light-emitting devices (FOLEDs) is preventing exposure of the active organic materials to water vapour and oxygen [1]. For the application of a FOLED, the required water vapour transmission rate (WVTR) of the barrier layers must be less than 10^{-6} g/m^2·day [2]. For a barrier layer with a low WVTR, inorganic materials such as metal, aluminium oxide (Al_2O_3) and silicon oxide are preferred [3]. Organic and inorganic multi-barrier layer coatings have delivered high performances, in the blocking of water vapour [4]. However, there is no commercially available method that can be applicable to a FOLED for the measurement of a sample barrier layer that has a very low WVTR.

To measure the WVTR for barrier layers, several methods have been reported. The MOCON, Inc. (Minnesota, USA) test has been used as a standard for WVTR measurement for more than 40 years. When testing the WVTR, flat film sample material is placed in a test cell. The test cell is divided into two chambers separated by the sample material. The WVTR is calculated from the molecules of water diffused through the sample material. However, the MOCON test is limited to the measurement of WVTRs that exceed 5×10^{-3} g/m^2·day [5]. There is a calcium (Ca) degradation test that can be used to determine the low permeation rate for a barrier layer. In this test, metallic Ca film is encapsulated by a barrier film and its transparency [6], or electrical conductivity [7], is monitored according to the water vapour and oxygen penetration through the barrier film. In the Ca degradation test, however, the individual contribution of water vapour and oxygen to the degradation of the Ca film has not been clearly distinguished. Choi *et al.* [8] reported a Tritium test whereby a radioactive isotope of water is used to measure values of the WVTR as low as approximately 10^{-6} g/m^2·day. Unfortunately, this Tritium test uses a radioactive isotope. Therefore, the Tritium test is not commercially viable.

Fortunately, in the vacuum-related research and industrial fields, a helium (He) leak detector has been widely used to find leaks in vacuum equipment [9]. He leak detectors may also be used to measure the permeability of microsized porous materials. In addition, He is non-toxic and is considered the second-lightest element. Furthermore, He has a very small kinetic diameter of 0.26 nm [10]. The lightness of weight and the small diameter of He could be important in improving measurement sensitivity in the permeability of a barrier layer. To achieve that outcome, the use of an He leak detector to conduct a systematic study on the permeation properties of He through barrier layers is required.

In the work reported in this Letter, we used an He leak detector to demonstrate a novel permeation test for metallic barrier layers. The measured values from the He detector test were compared with the results from a conventional MOCON test. Aluminium (Al) and chromium (Cr) thin films in a nanometre range of thicknesses were deposited onto polyethylene terephthalate (PET) substrates by magnetron sputtering. The values of He permeation through the samples were monitored using the He detector test. The results were compared with the images observed by field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM).

2. Experimental details: As a barrier layer for water vapour, Al or Cr film was deposited onto a PET substrate using a DC-magnetron sputtering system. The thicknesses of the metallic coating layers in the samples were varied from 200 to 1000 nm. Thicknesses of the PET substrates approximated 180 µm. The water-vapour permeability of the samples was measured using a conventional MOCON test. The deposition parameters during the sputter process and the measurement conditions for the MOCON test were reported in a previous work [11]. In this Letter, a novel method, an He leak detector (Varian PRO2), was used to test the permeation of the barrier layers.

Fig. 1 shows a schematic diagram and photograph of the He leak detector used in this work. As shown in Fig. 1*a*, the system has two chambers such as chamber 1 and chamber 2. The sample was installed in the boundary region of the two chambers, as shown in Fig. 1*b*. The operation principle of this system is similar to that of an He leak detector. First, the sample was positioned on the O-ring portion, as shown in Fig. 1*b*, and clamped to contact the two chambers. In the closed state of valve 1 (V_1), chamber 1 and chamber 2 could be evacuated using a vacuum pump. When the pressure reached a range of 10^{-5} Torr, valve 2 was closed. In the next step, when valve 1 was opened, He flowed into chamber 1 and permeated through the sample. When the He permeated into chamber 2, the He pressure in chamber 2 was increased proportion to the amount of He that had penetrated the samples.

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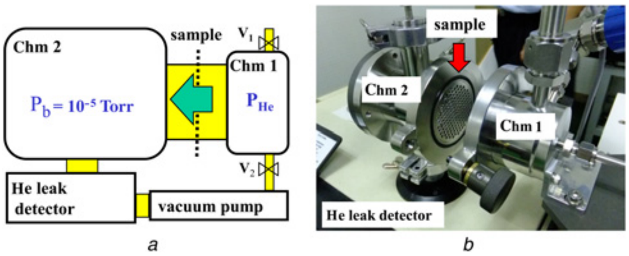

Figure 1 *Experimental setup for the He detector test in this work*
a Schematic diagram of the He detector test unit
b Photograph of the He detector test unit focused on a sample position
Chm 1 and Chm 2 denote chamber 1 and chamber 2, respectively
Volume of chamber 1 and chamber 2 was 244 and 120 cc, respectively

According to the results of the MOCON and He-detector testing, the gauge sizes of the samples were 25 and 70 mm in diameter, respectively. The temperature for the MOCON test was 37.8°C, while the He detector test could be conducted at room temperature. FESEM (S-4800, HITACHI) and conventional AFM (SII Nano Technology Inc.) were used to examine the surface morphology, or microstructure, of the samples.

3. Results and discussion: Fig. 2*a* shows the PET substrate and representative samples. The thicknesses of the Al film on the PET substrates were 0, 200 and 1000 nm, respectively. Fig. 2*b* shows the change in He pressure in chamber 2 against the permeation time of He through the sample. As we expected, the initial pressure of He in chamber 2 was in the range of 10^{-10} Torr. For the samples with no Al film and that with 100 nm thick Al film on the PET, a rise in the pressure of He was clearly detected in chamber 2 with values after saturation that measured 1.1×10^{-5} and 3.1×10^{-6} Torr, respectively, as a result of He permeating the samples. Meanwhile, the Al foil sample with 30 µm in thickness showed no change in He pressure, which indicated almost no permeation.

Table 1 shows the values of WVTR as measured by the MOCON test and He pressure as measured by the He detector test in chamber 2. The permeation properties, as measured by the MOCON and He detector tests for samples with Al coating on the PET, showed similar trends. It is worth noting that the high values of He pressure in the He detector test indicate poor permeation blocking properties for the barrier layer. The permeation blocking properties increased exponentially with an increase in the Al coating thickness. The results shown in Table 1 point out two noteworthy facts. First, the WVTR for the 200 nm thick Al and Cr films on the PET substrate showed large differences in values: 0.83 and 6.13 g/m^2·day, respectively. Secondly, the WVTR values were the same (5×10^{-3} g/m^2) for the samples with 1000 nm thick Al coating on the PET substrate and for Al foil.

Compared with the WVTR from the MOCON test, the He pressure as measured by the He detector test showed a wider range of values (from 1.1×10^{-10} to 1.1×10^{-5} Torr). The minimum value for He pressure was 1.1×10^{-10} Torr for the Al foil, and the maximum value from the PET substrate was 1.1×10^{-5} Torr. For the samples with 200 and 1000 nm thick Al coatings on the PET substrate, the values for He pressure were 3.1×10^{-6} and 3.2×10^{-8} Torr, respectively. However, He pressure for the Al foil showed 1.1×10^{-10} Torr. The different values in He pressure from the two samples, Al coating (1000 nm) and Al foil (30 µm), indicated that the He detector test could be used to measure the permeation properties of barrier layer samples that have very low values. From the results shown in Table 1 and in Fig. 2*b*, we can conclude that the MOCON test was limited to the measurement of values for WVTR that were less than 5×10^{-3} g/m^2. The low sensitivity for the permeation properties of the MOCON test may have been because of the nature of large water clusters that are composed of a few tenths of H_2O molecules in the gas phase [12].

It is also worthwhile to compare the properties of the barrier layers of the two samples that had 200 nm thick coats of Al and Cr on PET substrates in Table 1. As measured by the MOCON and He detection tests, the permeation blocking properties of the Cr film were much poorer than those of the Al film. Furthermore, the permeation blocking properties for the sample with 200 nm thick Cr coating were comparable to those of the PET substrates. The poor permeation blocking properties for the samples with Cr film should be explained by further study. Therefore, a study on the relationship between the microstructure and permeation blocking properties of samples is necessary.

Fig. 3 shows the SEM photographs of samples with a 200 nm thick Cr film coating on a PET substrate. As shown in Fig. 3*a*, microcracks can be observed in the Cr film. However, no remarkable microcracks could be observed in the Al film on the PET substrates. The microcracks in the Cr film on the PET substrates may have caused poor permeation blocking properties of Cr coating

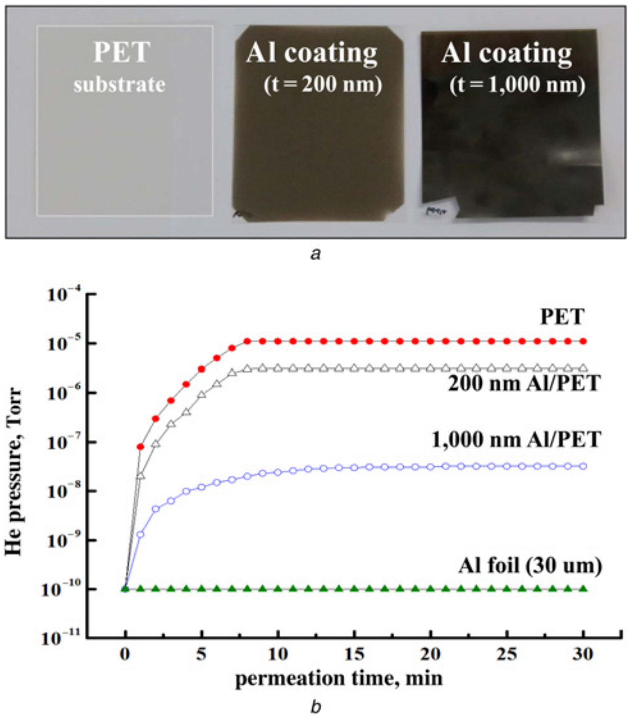

Figure 2 *Photographs of test samples and He pressure rise curves*
a Three different samples
b Change of He pressure dependence on permeation time for different samples, as shown in Table 1

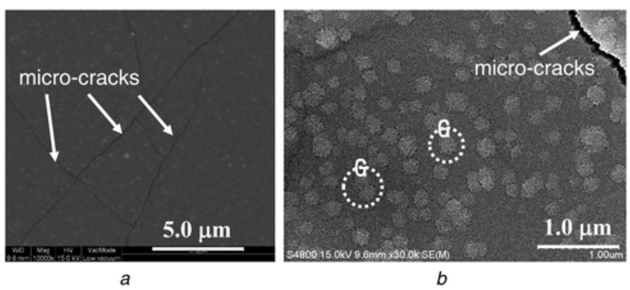

Figure 3 *SEM image of a sample with a 200 nm thick Cr coating on the PET substrate*
a Area around microcracks (×10 000)
b Area far from microcracks (×30 000)

Table 1 Permeation properties as measured by the MOCON test and the He detector test for different samples

Specimen	WVTR, g/m^2·day	He pressure, Torr
PET substrate	9.45	1.1×10^{-5}
Al (200 nm)/PET	0.83	3.1×10^{-6}
Al (1000 nm)/PET	5.2×10^{-3}	3.2×10^{-8}
Al foil (30 μm)	5.3×10^{-3}	1.1×10^{-10}
Cr (200 nm)/PET	6.13	1.3×10^{-5}

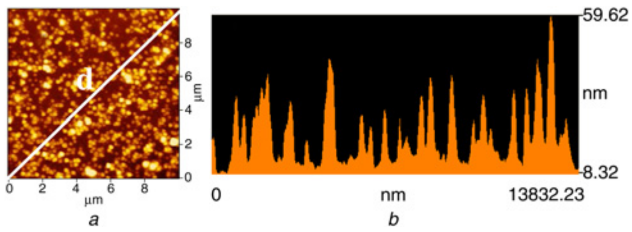

Figure 4 *AFM results for a sample with a 200 nm thick Cr coating on the PET substrate*
a AFM image
b Roughness profile from line 'd' in Fig. 4*a*

shown in Table 1. From the SEM image in Fig. 3*b*, a number of island-shaped regions (G) can be observed in the Cr film. To help examine the differences between the 'G' region and the neighbouring continuous region, a high-resolution SEM image was taken. However, no clear result could be obtained.

For a better understanding into the nature of the Cr coating on a PET substrate, an AFM observation was performed. Fig. 4 shows the AFM results for Cr film coating that was 200 nm thick. The AFM image and surface roughness profile appear along the lines marked 'd' in Fig. 4*a*. The maximum difference in height calculated from the apex minus the valley in the profile peaks was calculated to be approximately 50 nm. No special microsized defects such as pinholes or voids were observed. Therefore it was concluded that the permeation mechanism of He or water vapour through the overall samples could have been the result of a diffusion process [11]. The poor permeation blocking properties of Cr film on the PET substrates was because of an accelerated diffusion process of He or water vapour through microcracks.

The gas permeation properties through a barrier layer can be explained by considering two factors: the solubility coefficient and the diffusion coefficient [13]. In this work, a novel permeation test for metallic barrier layers was investigated using an He leak detector to estimate the high sensitivity in permeation properties that could be applicable to FOLEDs. The He detector test provided high-resolution He pressure for samples showing a high degree of water vapour blockage. The high-sensitivity permeation properties of barrier layers shown by the He detector test were because of both the lightness of weight and the small size of He [14]. These two properties of He accelerated its diffusion through the samples. Finally, the He detector test showed potential for its use in the development of long-life FOLEDs by measuring the water vapour permeation blocking properties of barrier layers.

4. Conclusion: A novel permeation test for metallic barrier layers incorporated an He leak detector to evaluate the gas permeation properties. Compared with the WVTR from a conventional MOCON test, the values of He pressure produced by the He detector test showed much wider ranges and conveyed a high sensitivity to permeation properties. The permeation blocking properties of Cr film on PET substrates were much poorer than those for Al film under the same conditions. The poor permeation blocking of the Cr film was because of an accelerated diffusion process of He or water vapour through microcracks in the Cr film. The high sensitivity to permeation properties that were possible using the He detector test resulted from a combination of the lightness of weight and the small size of He, which accelerated its diffusion through the barrier layers. The He detector test described in this work will be used in the development of long-life FOLEDs to measure the permeation properties of water vapour for barrier layers with a low WVTR.

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6 References

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