LOMSS

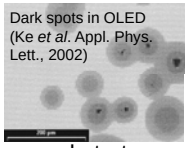
Analytical Studies on Gas Transport in Inorganic/Organic Hybrid Barrier Structures

Objectives:

- To gain understanding of the physics in gas transport through nanometer to micrometer scale inorganic/organic hybrid barrier structures
- To develop multiscale gas transport models through analytical and numerical approaches
- Ultimately, to develop high performance barrier films for flexible organic device applications

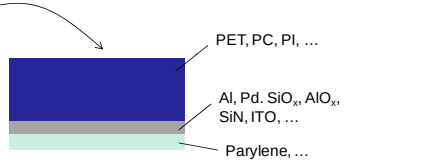
Barrier films for flexible organic devices

- Ingress of oxygen and water vapor causes degradation of organic charge carriers as well as oxidation at the organic-cathode interface, resulting in dark spots and pixel shrinkage in organic light-emitting diodes (OLED) and in deterioration of power conversion efficiency of organic solar cells.



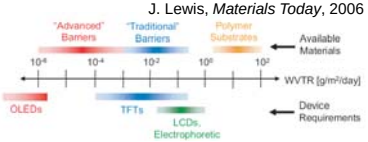
- The active layers of the devices must be encapsulated by polymer substrates coated with metallic/ceramic films to reduce or eliminate gas transport.


4" flexible transparent OLED from University Display and LG



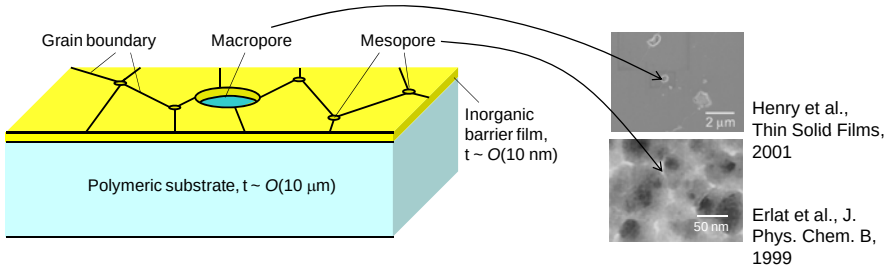
J. Lewis, *Materials Today*, 2006

- The requirement of barrier performance is much severer for organic electronics than for traditional applications (e.g., food).



Knowledge of gas transport mechanisms is crucial to development and/or improvement of barrier systems and corresponding life prediction models.

What is happening in barrier films?



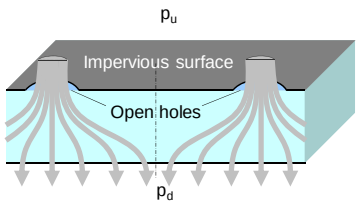
Henry et al., Thin Solid Films, 2001

Erlat et al., J. Phys. Chem. B, 1999

- Polymer substrate: Fickian or non-Fickian gas diffusion
- Macropores (d = 50 nm ~ several μm): viscous flow; virtually no resistance to gas transport compared to gas diffusion in polymer
- Mesopores (d = 0.5 ~ 5 nm): molecular flow, capillary condensation and adsorption (and more?)
- Solid part of the barrier film: diffusion of small gas species such as hydrogen (in general negligible). Possibly water vapor transport by chemical decomposition and re-combination across the film (Erlat et al., J. Chem. Phys. B, 2004).

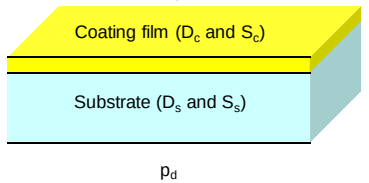
Existing gas transport models

Open-hole model



- Inorganic barrier layer is modeled as an impervious surface with open pinholes.
- Deals with gas transport through macropores only
- Suitable for studying micrometer scale phenomena
- Tremendous cost for numerical modeling of even a single-hole case.
- Essentially, it is not sufficient to explain true phenomena since it is not able to treat mesopores properly (d ~ nm).

Ideal laminate theory (ILT)-based model



- Inorganic barrier layer is modeled as a fictitious polymer layer with effective gas diffusion properties.
- Gas transport through macro- and meso-pores are smeared on the effective properties.
- Suitable for macroscopic scale modeling (e.g., true device scale).
- Effective permeability can be determined from a gas transmission test. However, measurement of other properties such as solubility is extremely difficult.

Analytical solution for ILT-based model(1,2)

Mass continuity at the entire film can be approximated as

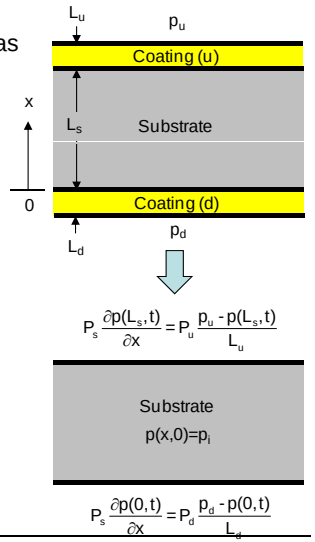
$$-D_c S_c \frac{p_{amb} - p_{int}}{L_c}\delta t \approx \delta p\left(S_c L_c + S_s L_s\right)$$

p: pressure, D: Diffusivity, S: solubility

L: thickness; subscripts *c:* coating, *s*: substrate, *amb*: ambient, *int*: interface

In general, $L_c S_c << L_s S_s$ for barrier film-coated polymer substrates, yielding

$$\frac{\delta p}{\delta t} \propto \frac{D_c S_c}{L_c L_s S_s} = A\left(D_c S_c\right) = A \cdot P_c \quad \text{where} \quad A = \frac{1}{L_c L_s S_s}$$



Analytical solution for ILT-based model(1,2)

It shows that the permeability of the coating layer dominates the water diffusion behavior of the bi-layer film and thus the solubility does not have to be measured accurately. This can be viewed physically as a negligible amount of gas absorbed in the barrier film compared to that in the polymer substrate. Thus, the bilayer problem can be treated as a single layer problem with a "convective" boundary condition. The analytical solution for the general case shown in the right figure can be derived as below:

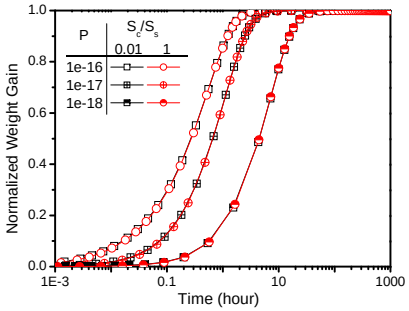
$$p(x,t) = a_1 + a_2 x + \sum_{n=1}^{\infty} A_n \left[\sin\left(\lambda_n x\right) + \frac{\lambda_n L_s}{H_d}\cos\left(\lambda_n x\right)\right]\exp\left(-\lambda_n{}^2 D_s t\right)$$

where $\lambda_n L_s\left(H_u + H_d\right)\cos\left(\lambda_n L_s\right) + \left[H_u H_d - \left(\lambda_n L_s\right)^2\right]\sin\left(\lambda_n L_s\right) = 0$ $\qquad H_u = \frac{P_u L_s}{P_s L_u}$ and $H_d = \frac{P_d L_s}{P_s L_d}$

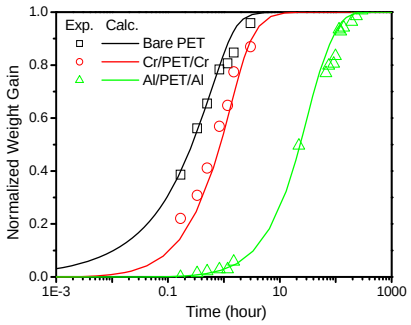
$$a_1 = \frac{H_u H_d p_d + H_u p_u + H_d p_d}{H_u H_d + H_u + H_d} \quad \text{and} \quad a_2 = \frac{1}{L_s}\frac{H_u H_d\left(p_u - p_d\right)}{H_u H_d + H_u + H_d}$$

$$A_n = 2\frac{H_d{}^2\left(p_i - p_d\right) - H_u H_d \frac{H_d{}^2 + \left(\lambda_n L_s\right)^2}{H_u H_d - \left(\lambda_n L_s\right)^2}\left(p_i - p_u\right)\cos\left(\lambda_n L_s\right)}{\lambda_n L_s\left[H_d{}^2 + H_d + \left(\lambda_n L\right)^2\right] - H_d \lambda_n L_s \cos\left(2\lambda_n L_s\right) + \frac{1}{2}\left[\left(\lambda_n L_s\right)^2 - H_d{}^2\right]\sin\left(2\lambda_n L\right)}$$

Analytical solution for ILT-based model(1,2)



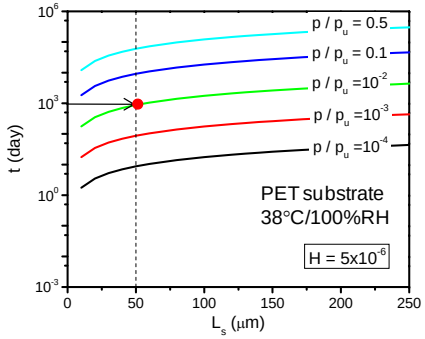
Validation of simplified model with actual ILT model



Validation of simplified model with experimental measurement of water ingress

Implications from the analytical solution(2)

Shelf life prediction



The time required for a gas to reach a critical pressure, p_c, at the active layer (or shelf life) can be expressed in terms of the gas transmission rate (J_{cs}; WVTR or OTR) as

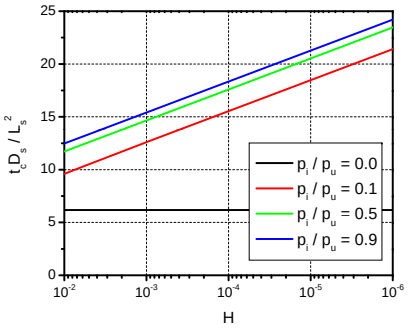
$$t_{shelf} = -\frac{P_s p_u}{J_{cs}}\frac{L_s}{D_s}\ln\left(1 - \frac{p_c}{p_u}\right)$$

If we assume a required shelf life is 1000 days, it reveals that the critical pressure is approximately $0.01p_u$. *Inversely, if we know the critical pressure at the active layer, the critical GTR can be re-defined for a required shelf life as*

$$J_{cs} = -\frac{P_s p_u}{t_d}\frac{L_s}{D_s}\ln\left(1 - \frac{p_c}{p_u}\right)$$

Implications from the analytical solution(2)

Stabilization time for gas transmission testing



If a specimen is not fully dried or degassed before GTR testing, the initial pressure affects the stabilization time. The analytical solution for normalized gas transmission rate $(\tilde{J}_{cs})$ is expressed for high performance films (H < 0.01) as

$$\tilde{J}_{cs} \approx 1 + 2\left[\frac{p_i}{Hp_u} + \frac{2}{\pi}\left(\frac{p_i}{p_u} - 1\right)\right]\exp\left[-\left(\frac{\pi}{2L_s}\right)^2 D_s t\right]$$

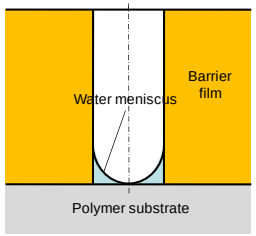
Obviously, the transient gas transmission behavior becomes a function of H. The stabilization time is then approximated as $(\tilde{J}_{cs} = 1.01)$

$$t_s \approx \frac{4L_s^2}{\pi^2 D_s}\left\{5.298 + \ln\left[\frac{p_i}{Hp_u} + \frac{2}{\pi}\left(\frac{p_i}{p_u} - 1\right)\right]\right\}$$

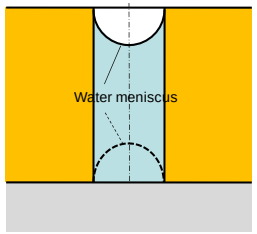
Mesopore blockage by water condensation(3)

Water condensation takes place inside mesopores (d = 0.5 ~ 5 nm) through adsorption and capillary condensation. It can change the gas transport behavior in two ways:

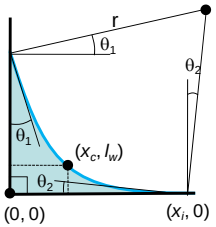
- Condensed water hinders other gases from transporting through mesopores
- Its presence also changes the water diffusion behavior into the polymer substrate because the vapor and the liquid phase show different diffusion behaviors



Bottom wall covering mode



Bulk condensation mode



Geometry of covering mode

Mesopore blockage by water condensation(3)

The Kelvin equation is not able to properly predict the behavior of water condensation due to:

- the effect of molecular interactions, which are localized and discrete by nature
- the sub-molecular scale of meniscus tip

By accounting for these effects, analytical solutions are obtained as:

Critical relative humidity for bulk capillary condensation:

$$h_c = \exp\left[-\frac{c\gamma V\cos\theta_1}{(r_p - t_w)R_0T}\right]$$

Critical relative humidity for full bottom wall covering:

$$h_{c,bsc} = \exp\left[-\frac{c\gamma V(\cos\theta_1 - \sin\theta_2)}{(r_p - t_w - L/2)R_0T}\right]$$

c: 1 for flat, 2 for circular
γ: surface tension, V: molar volume
r_p: pore radius or half width
t_w: adsorption thickness,
L: molecular spacing in liquid phase

Mesopore blockage by water condensation(3)

An analytical solution for the partial covering extent (n_c) can be derived in the form of a combination of geometric and thermodynamic meniscus tips as

$$n_c(h) = n_{c,g}(h) + \left(\frac{h}{h_{c,bsc}}\right)^2\left[n_{c,t}(h) - n_{c,g}(h)\right]$$

Geometric meniscus tip:

$$n_{c,g} = \frac{t_w}{r_p} - \frac{c\gamma V(\cos\theta_1 - \sin\theta_2)}{r_p R_0 T\ln h} - \frac{L}{2r_p}\cot\left(\frac{\alpha}{2} + \theta_2\right)$$

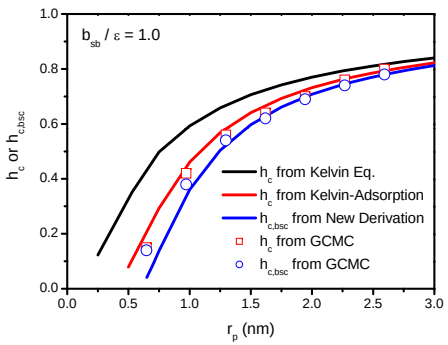
where $$-\frac{c\gamma V\left[\cos\theta_2 - \cos(\theta_2 + \alpha)\right]}{R_0T\ln h} = l_w$$

Thermodynamic meniscus tip:

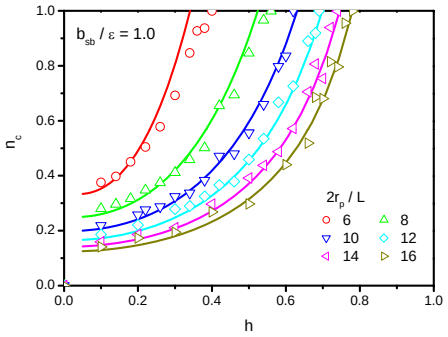
$$n_{c,t} = \frac{t_w}{r_p - L/2} - \frac{c\gamma V(\cos\theta_1 - \sin\theta_2)}{(r_p - L/2)R_0T\ln h}$$

Mesopore blockage by water condensation(3)

The derived analytical equations agree well with Grand Canonical Monte Carlo (GCMC) simulations using a gas lattice model.



Comparison of critical relative humidity



Comparison of meniscus tip evolution (lines: analytical equation, symbols: GCMC)

Ongoing and Future work

- To understand the physics of other phenomena in mesopores and model them properly
- To improve the open-hole model by incorporating physical models for phenomena in mesopores
- To link microscopic models with macroscopic models to establish a comprehensive modeling scheme for gas transport analysis of barrier films

Publications

1) C. Jang, Y.-R. Cho and B. Han, “Ideal Laminate Theory for Water Transport Analysis of Metal-Coated Polymer Films,” Applied Physics Letters, Vo. 93, 133307, 2008.

2) C. Jang and B. Han, “Analytical Solutions of Gas Transport Problems in Inorganic/Organic Hybrid Structure for Gas Barrier Applications,” Journal of Applied Physics, Vol. 105, 093532, 2009.

3) C. Jang and B. Han, “Analytical and Molecular Simulation Study of Water Condensation in Mesopores with Closed Ends,” Journal of Chemical Physics, in press, Vol. 132, 2010.