NREL’s e-Ca Test

Barrier Technologies Workshop

Arrelaine A. Dameron

September 19, 2012
Characterization of Water Permeation Barriers

Desire a characterization method that is:

- Reproducible
- Highly sensitive
- Easy to use
- Scalable
### Application Specific Tolerable Water Permeation

<table>
<thead>
<tr>
<th>Volume in 1 m² after 20 yrs</th>
<th>WVTR (g/m²/day)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>~7 L</td>
<td>1</td>
<td>Food Packaging</td>
</tr>
<tr>
<td>0.1</td>
<td>LCDs</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>TFTs</td>
<td></td>
</tr>
<tr>
<td>10⁻³</td>
<td>CdTe /Thin Film</td>
<td></td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>CIGS</td>
<td></td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>OPV &amp; OLEDs</td>
<td></td>
</tr>
<tr>
<td>10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻⁻⁷</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Gravimetric Test Limit**
  - ASTM E96
    - (~1 x 10⁻¹)
  - Test Limit: ~5 x 10⁻⁷ g/m²/day
- **Isostatic Test Limit**
  - ASTM F1249
    - (~5 x 10⁻⁴)
  - Test Limit: ~7 mL
- **e-Ca Test Limit**
  - (~5 x 10⁻⁷)
  - Test Limit: ~7 μL
Ca Test Basics

\[ \text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2 \]

Opaque and Conductive $\rightarrow$ Transparent and Insulating

Optical Characterization:
- Visual evaluation
- Pinhole identification

Electrical Characterization:
- Greater range of sensitivity
- Ease of Use
- Scalability & Throughput

NREL’s e-Ca Test

Ca +$2\text{H}_2\text{O}(g) \rightarrow \text{Ca(OH)}_2 + \text{H}_2$

Ca transforms from opaque, conductive metal to transparent, resistive oxide upon exposure to water.
We measure the resistance with respect to time to calculate the WVTR.
Samples on test
Actual measured data from a barrier film provided by a commercial partner shows steady state permeation at \(~3 \times 10^{-5}\) g/m²/day. This data is well above the sensitivity limits of NREL’s e-Ca test.
Ca Test Components

- **Computer for Data collection**
  - Custom software
    - Data collection, averaging and calculations, and WVTR display
- **Commercial digital multimeter**
  - 6.5 digit accuracy => ±0.1 mΩ
- **Multiplexing Distribution Hardware**
  - Combination of commercially available and custom assembled instrumentation
  - Current configuration can measure up to 128 samples
- **Ca Test Assembly**
  - Cables between electronics and Ca assembly
  - Commercial edgocard connector for easy/fast connect/disconnect
  - **Custom Test Card with Ca and Au traces**
    - Evaporated contacts using shadow mask onto glass substrate
  - Commercial edgeseal
  - **Custom diffusion spacer element**
    - Machined aluminum block
  - Barrier Film
Test Card

- Ca Traces are fabricated separate from the barrier film
- 3 redundant 4-pt measurements of Ca resistance as a function of time
- Witness line monitors edgeseal integrity and provides internal standard of sensitivity limits
- Inert contacts pass signal to the outside of the assembly and fit into standard edgecard connector
Test Card Fabrication
Test card stability and packaging

• Test cards can be produced in bulk (and stored in inert environment) prior to obtaining barriers to be tested.

• Storage in ambient conditions for 2 months using simple packaging methods resulted in <1% change (worst).

Equivalent to <1Å/day or WVTR of $\approx 10^{-9}$g/m²/day

We even shipped them to Japan!
Edge Seal Evaluation

Using the Optical Ca Test concept as an effective means of evaluating edge seal materials similar to applied environment

\[ X = K \sqrt{t} \]

**PDMS**

85°C/ 85 %RH

<table>
<thead>
<tr>
<th>0 h</th>
<th>3 h</th>
<th>4.5 h</th>
</tr>
</thead>
</table>

**Glass**

100nm Ca Edge Seal

Ca turns transparent appearing to shrink toward center
Typical Edgeseal Results

We tested for hundreds of hours....
Desiccant Filled PIB Edgesel

We tested for thousands of hours....
Relative Comparison of Materials

Finally we picked one! PIB#2 material performed the best and was the easiest to use for this application.
The ‘Spacer’

The spacer element is a non-absorbing mechanically fabricated cavity with apertures on the barrier side and on the test card side and sealing surfaces between the spacer to barrier film and spacer to the test card.

The spacer provides a means to assemble the test quickly with a mechanical press.

Addition of the spacer provides several advantages...
The ratio of apertures controls the sensitivity range by adjusting the barrier area relative to the Ca area.

- Some ratios (barrier area : Ca area) that we can use presently are 9:1, 30:1, 60:1, 700:1
Advantage #2: Diffusion compensation

- **Worst Case Scenario:** Ca traces are deposited onto the barrier but the barrier has a pinhole defect:

  - Resultant measurement is NOT reflective of the average WVTR!
Advantage #2: Accounting for defects

Without a spacer, the trace closest to the pinhole defect produced the highest WVTR.
Advantage #2: Accounting for defects

Without a spacer, the trace closest to the pinhole defect produced the highest WVTR.
Advantage #3: Edgeseal Control

- Spacer sealing surface design
  - allows for reproducible testing areas
  - limits the influence of the edgeseal materials on the measurement
Device to Device reproducibility

Aclar Standard @ 45C/85%RH WVTR

WVTR (g/m²/day)

Time (min)

- Witness WVTR
- Line #2 WVTR
- Aclar Standard @ 45C/85%RH WVTR
- NREL Line #1 WVTR
- NREL Line #3 WVTR
- Line #1 WVTR
- Line #3 WVTR
- NREL Witness WVTR
- NREL Line #2 WVTR
- NREL Aclar Standard @ 45C/85%RH WVTR
e-Ca Process Flowchart

1. Cut Glass
2. Clean Glass
3. Deposit Au
4. Deposit Ca
5. Cut Test Cards

Make Barrier Film

Dry out Barrier Film

Press Ca Test Assembly

Put Assembly on Test

Collect Data

Remove Assembly from Test

Remove Barrier

Recycle Spacer

Analyze Data

Calculate WVTR
Witness Correction and Data Averaging

Averaging over 1 hrs

Data Averaging Only

Averaging and Witness Correction

Witness WVTR
Line #1 WVTR
Line #2 WVTR
Line #3 WVTR
Average WVTR

Time (h)

WVTR (g/m²/day)
Witness Correction and Data Averaging

Averaging over 12 hrs

Data Averaging Only

Averaging and Witness Correction
Witness Correction and Data Averaging

Averaging over 24 hrs

Data Averaging Only

Averaging and Witness Correction

Witness WVTR
Line #1 WVTR
Line #2 WVTR
Line #3 WVTR
Average WVTR
Witness Correction and Data Averaging

Averaging over 48 hrs

Data Averaging Only

![Graph showing data averaging only]

Averaging and Witness Correction

![Graph showing averaging and witness correction]

Witness Correction and Data Averaging

Averaging over 48 hrs

Data Averaging Only

![Graph showing data averaging only]

Averaging and Witness Correction

![Graph showing averaging and witness correction]
Witness Correction and Data Averaging

Averaging over 120 hrs

Data Averaging Only

Averaging and Witness Correction

WVTR (g/m²/day)

Time (h)

Witness WVTR
Line #1 WVTR
Line #2 WVTR
Line #3 WVTR
Average WVTR
What we still need to do...

- Understanding Ca Test breakthrough and lag times
  - Ca degradation effects?
  - Spacer adsorption effects
  - Contact compatibility
  - Annealing effects
- Develop usable standards
Conclusions

• **e-Ca Test can be used *reproducibly* for a scalable *steady state* WVTR characterization method**

• **We have demonstrated measurement in the <10^{-5} g/m^2/day range and have confidence that 10^{-7} g/m^2/day can be qualitatively analyzed with this technique.**

• **Sensitivity can be modulated by:**
  - Varying aperture area
  - Temperature correction
  - Witness correction
  - Data Averaging

• **For accurate reproducible results, control of the spillover of edge seal material, and gas diffusion lengths are important.**