Calcium Test – Different test methods for WVTR on barriers, with an emphasis on ultrabarriers, sources of errors/irreproducibility, limits, etc. – basically why it's hard to do it right.

Matthew O. Reese, Michael D. Kempe, Arrelaine A. Dameron

AIMCAL

October 18, 2017

Outline

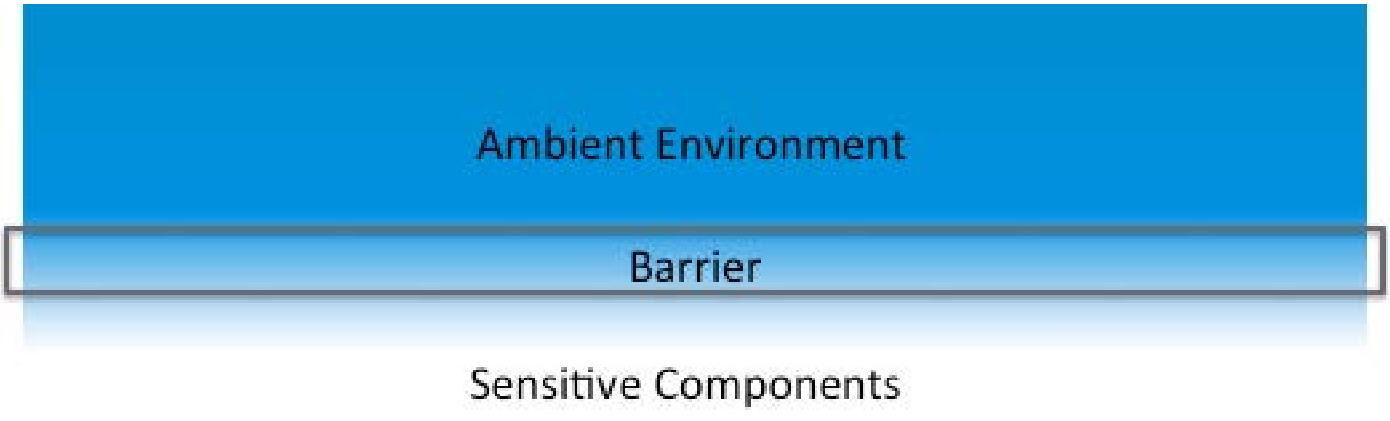
- **Understanding Water Vapor Transmission Rates (WVTR)**
- **How to measure WVTR**
- **NREL's electrical Ca (e-Ca) test**
- **Edge seal measurement**
- **WVTR standard development**

Introduction/Background

- **Many thin film PV technologies are sensitive to moisture requiring the use of packaging schemes that prevent or reduce moisture over a 25 y expected product lifetime.**
- **This is easily accomplished using a glass frontsheet, with an impermeable backsheet and polyisobutylene based edge seals.**
- **However, there is a desire to create modules with either a lightweight or flexible construction. This can be accomplished using a barrier film deposited on a flexible polymer substrate.**

Ascent Solar flexible module.

Characterization of Water Permeation Barriers



Vapor adsorbs and dissolves into barrier

Vapor diffuses

Vapor desorbs/outgasses

Desire a characterization method that is:

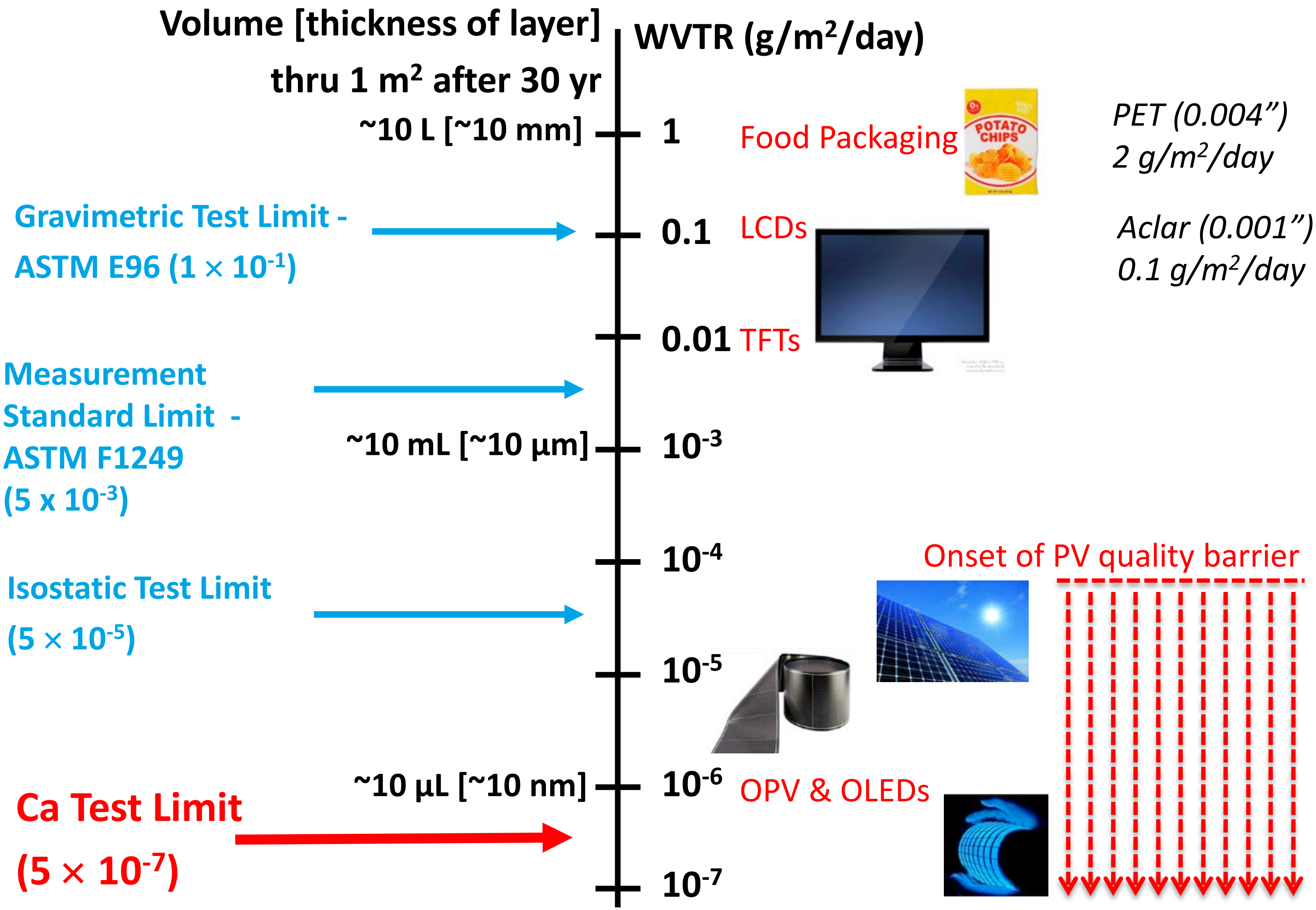
– Reproducible

– Highly sensitive

– Easy to use

– Scalable

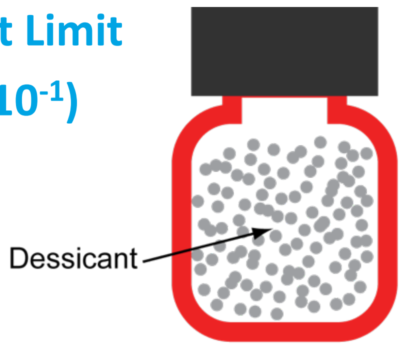
Water Vapor Transmission Rates (WVTR) Explained

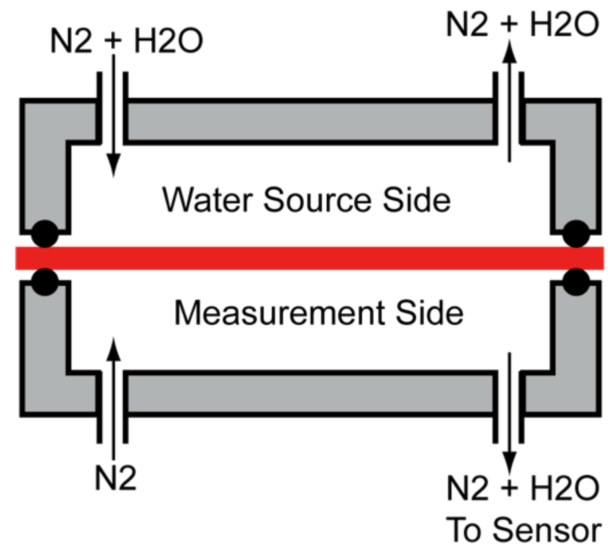


Methods to Measure WVTR: Cup & Isostatic

Gravimetric Test Limit

ASTM E96 (1×10^{-1})





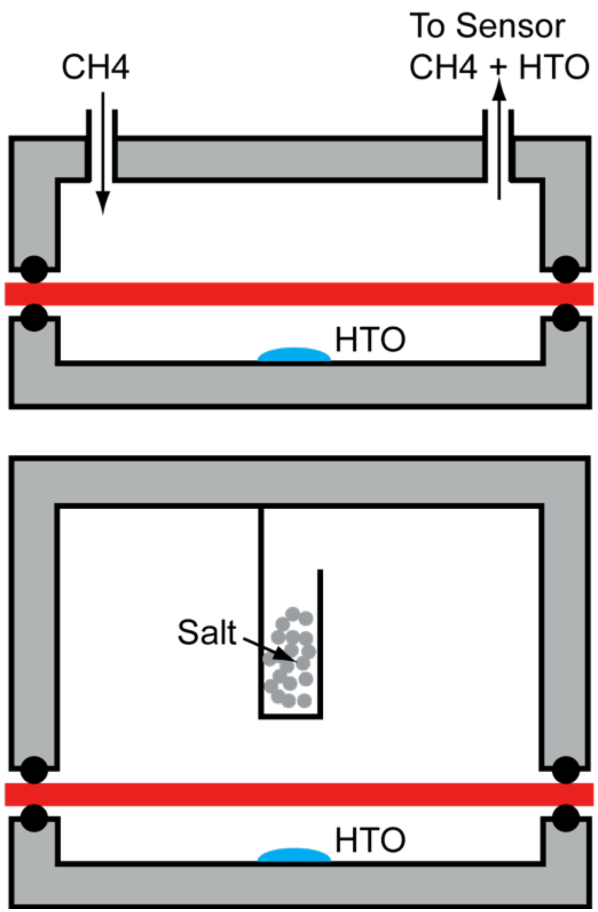
Isostatic Test

ASTM F1249 (5×10^{-3}) – Infrared detector

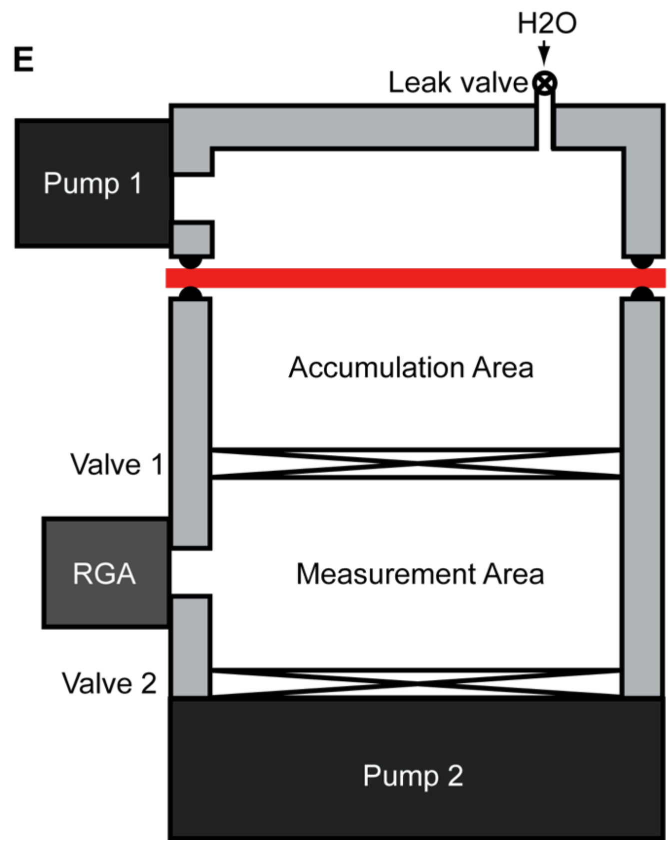
No standard (5×10^{-4}, 5×10^{-5}) – Coulometric detector

A.A. Dameron, M.O. Reese, T. Moricone, and M.D. Kempe "Understanding Moisture Ingress and Packaging Requirements for Photovoltaics", *Photovolt. Intl*. 5, 121 (2009).

Methods to Measure WVTR: HTO & Mass Spec.



HTO/Radioactive Tracer
No Standard ($<10^{-6}$ g/m^2/day)



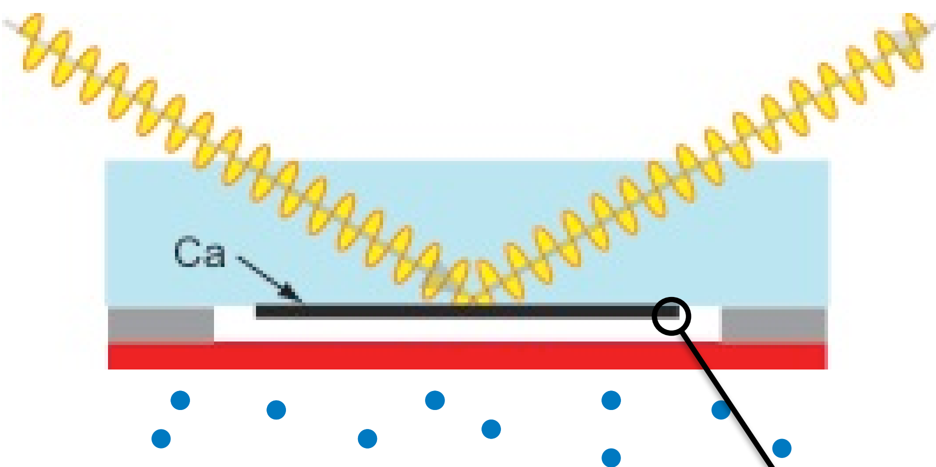
Mass Spectrometry
No Standard ($\sim10^{-7}$ g/m^2/day)

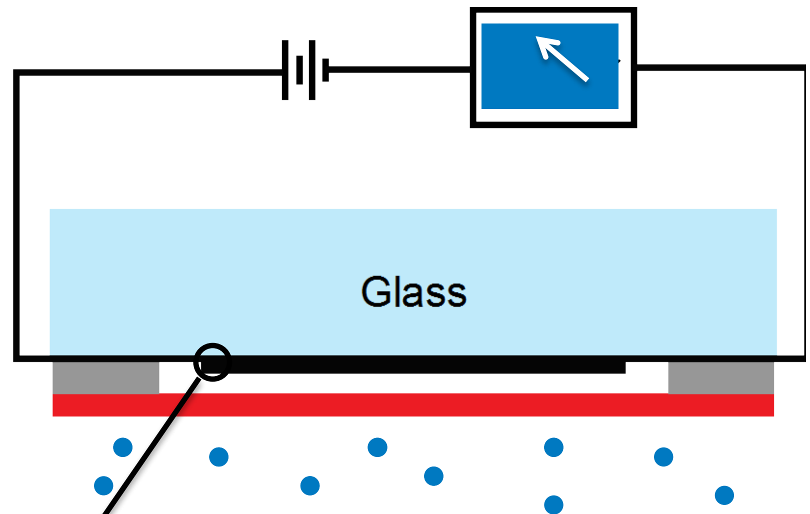
A.A. Dameron, M.O. Reese, T. Moricone, and M.D. Kempe “Understanding Moisture Ingress and Packaging Requirements for Photovoltaics”, *Photovolt. Intl*. 5, 121 (2009).

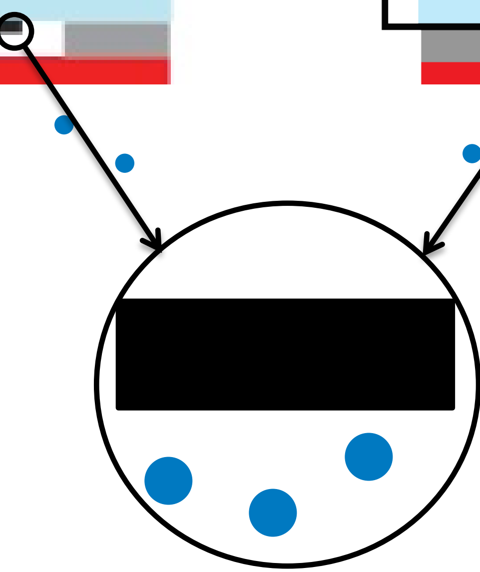
Methods to Measure WVTR: Ca Test

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

Opaque and Conductive → Transparent and Insulating







Optical Characterization:
- Visual evaluation
- Pinhole identification

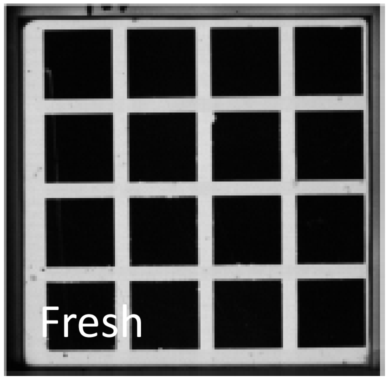
Electrical Characterization:
- Greater range of sensitivity
- Ease of Use
- Scalability & Throughput

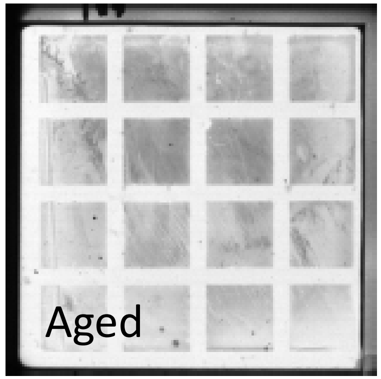
G.Nisato *et al.*, *Proceedings Asia Display/IDW* pp. 1435, 2001.

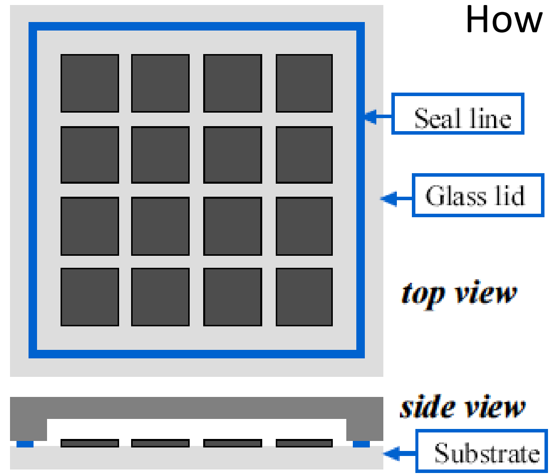
R. Paetzold *et al.*, *Review of Scientific Instruments*, vol. 74, pp. 5147, 2003.

Various Ca Test Methods: Original "Ca Test" – Optical

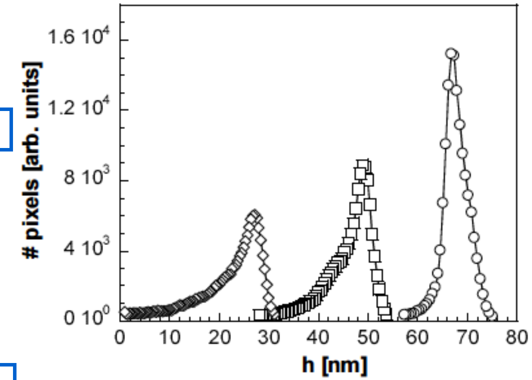
Transmission Mode (0.1 – 5×10^{-5} g/m^2/day)



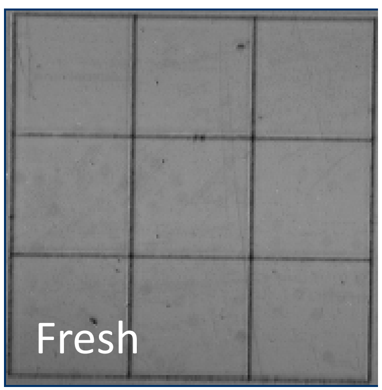


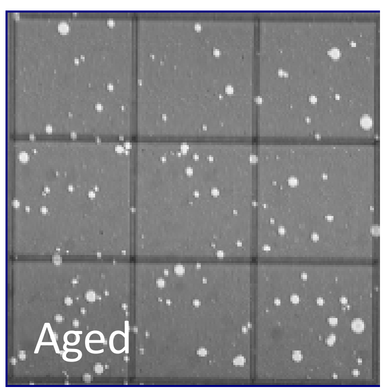


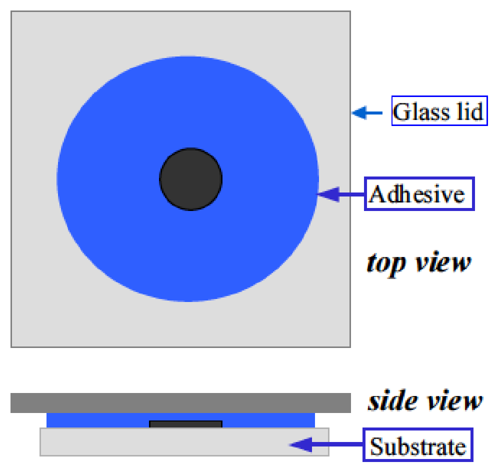
How fast does thickness change?



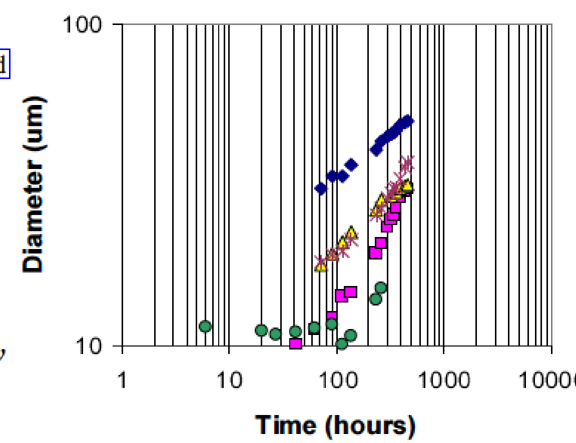
Reflectance Mode (4×10^{-7})







How fast do defects grow?

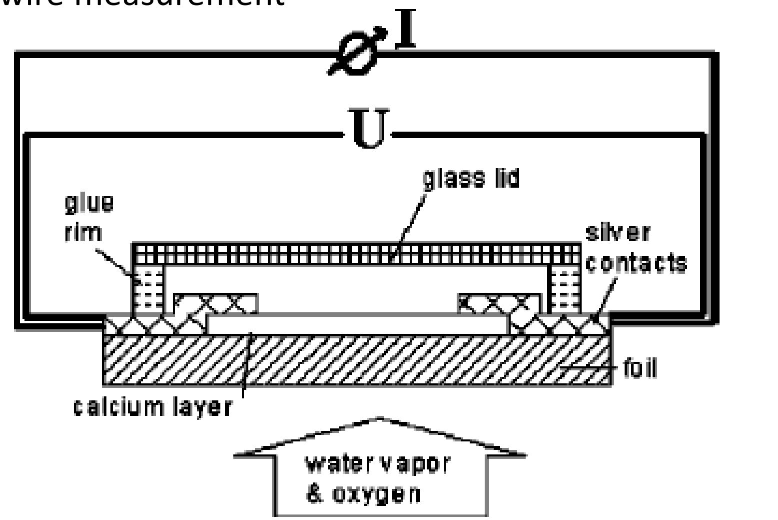


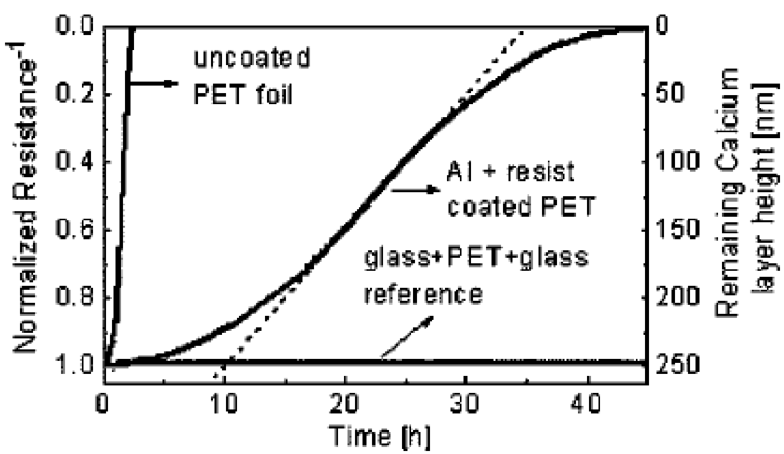
G.Nisato *et al.*, *Proceedings Asia Display/IDW* pp. 1435, 2001.

Various Ca Test Methods: “Ca Test” – Electrical

Paetzold, et al. (2003)
4-wire measurement

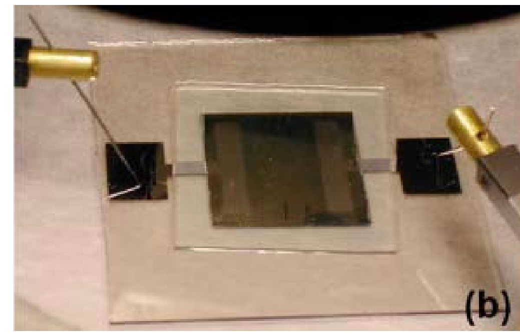
< 10^{-6} g/m^2/day

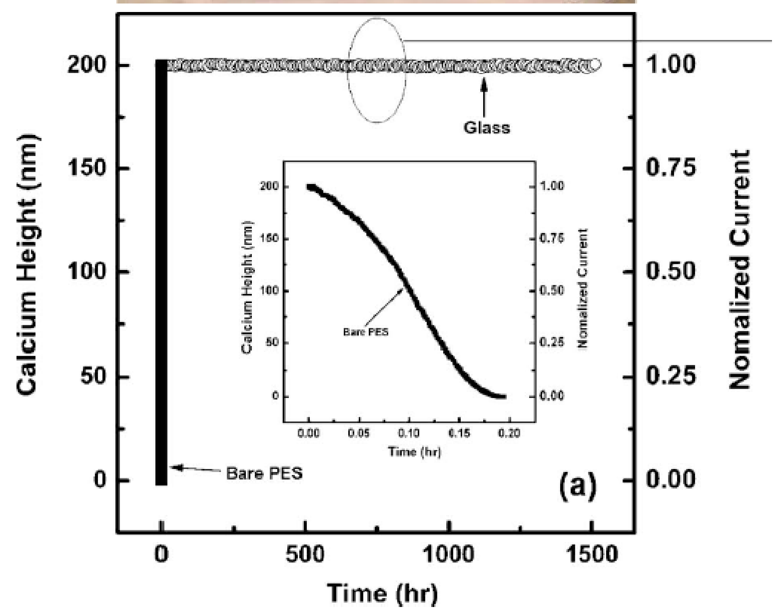




Choi, et al. (2007)
2-wire measurement

10 - 10^{-6} g/m^2/day

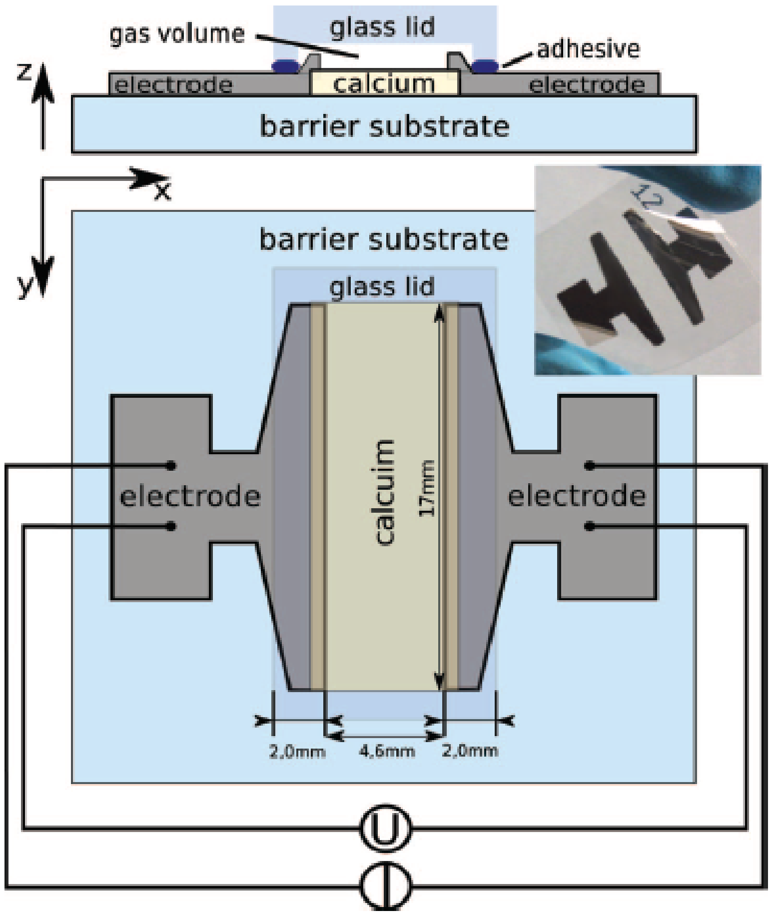


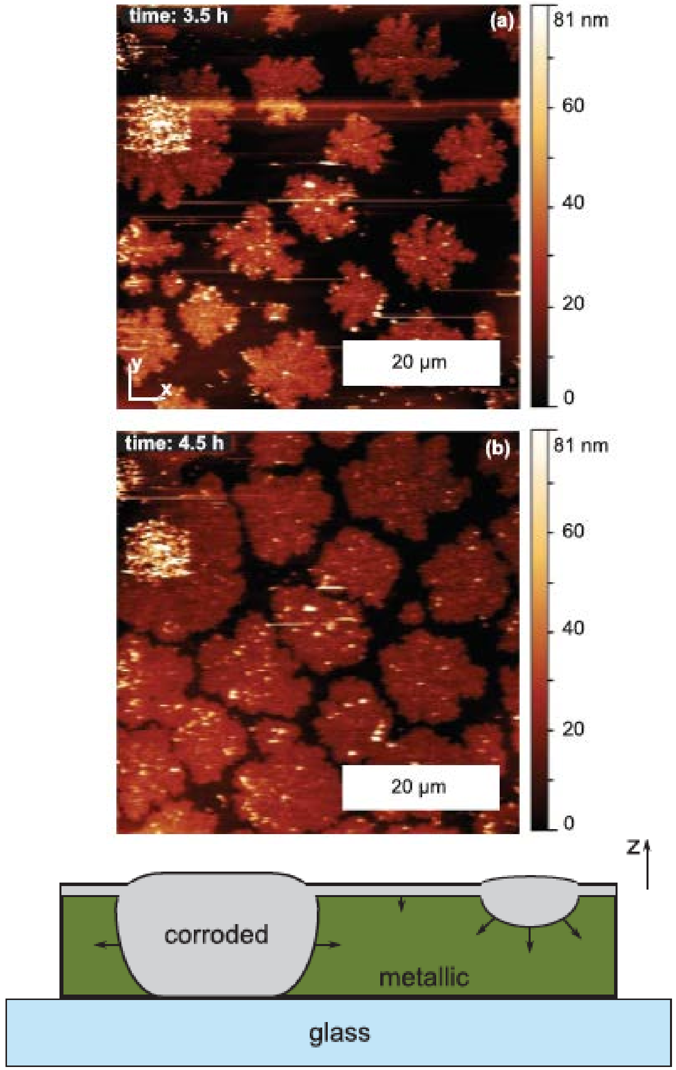


1. R. Paetzold *et al.*, *Review of Scientific Instruments*, vol. 74, pp. 5147, (2003).
2. J.H. Choi *et al. Review of Scientific Instruments*, vol. 78, pp. 064701 (2007).

Various Ca Test Methods: “Ca Test” – Electrical

Schubert et al. (2011) $15 - 10^{-5}$ g/m²/day

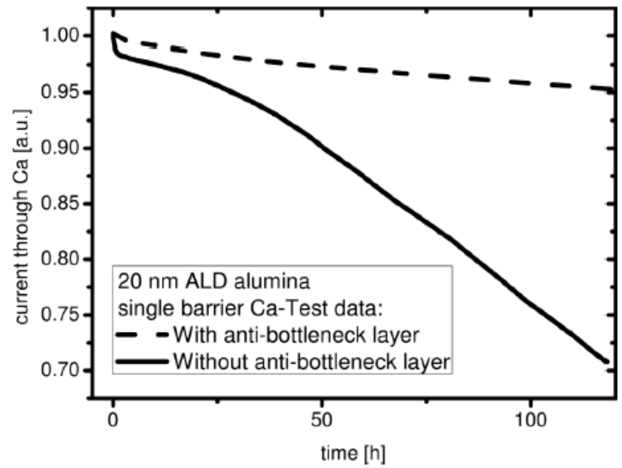


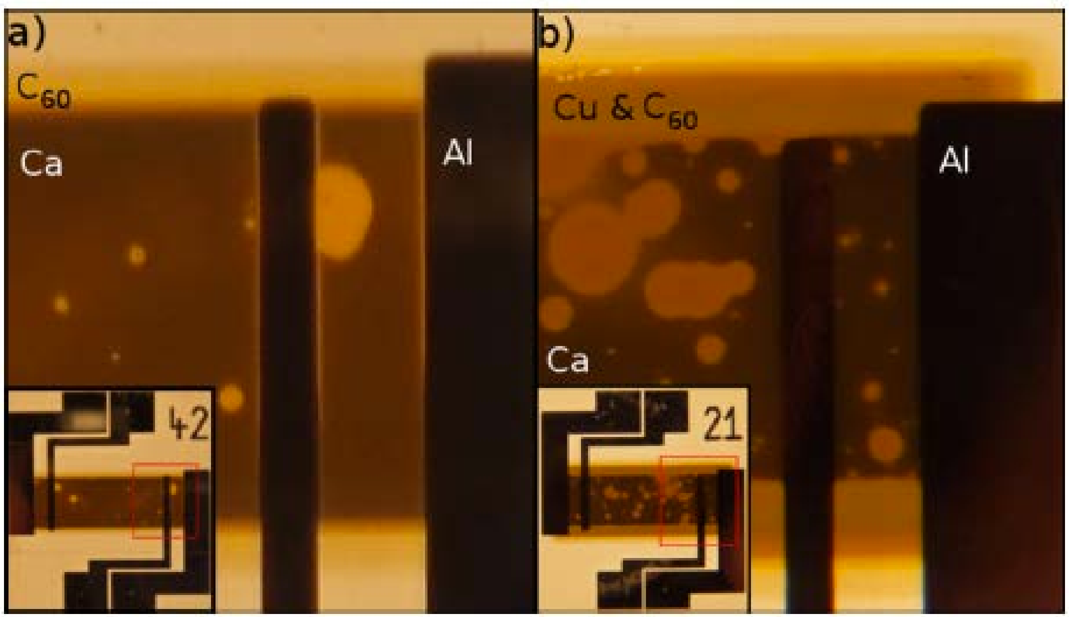


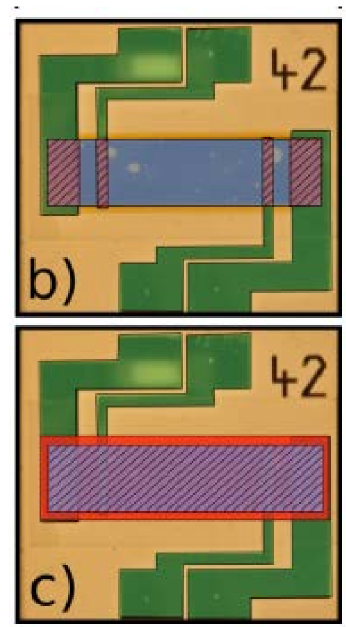
1. S. Schubert, H. Klumbies, L. Muller-Meskamp, K. Leo, *Rev. Sci. Instrum.* 82, 094101 (2011).
2. H. Klumbies, L. Muller-Meskamp, T. Monch, S. Schubert, K. Leo, *Rev. Sci. Instrum.* 84, 024103 (2013).
3. D.A. Nissen*, Oxidation of Metals* 11, 241 (1977).

Calcium Corrosion Effects

- **Contacts break at junction between the Ca and inert contact**
- **Electrochemical difference ($E_{0,Ca}$=-2.868 eV; $E_{0,Al}$=-1.662) drives corrosion of Ca**

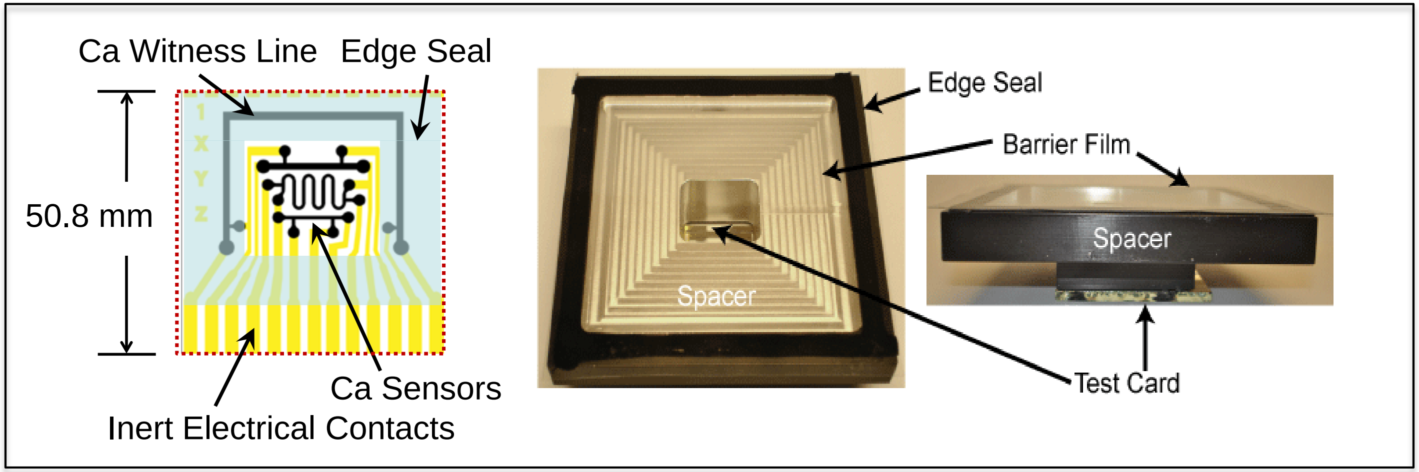






F. Nehm, L. Muller-Meskamp, H. Klumbies, K. Leo, *Rev. Sci. Instrum.* 86, 126110 (2015)

NREL’s e-Ca Test Components

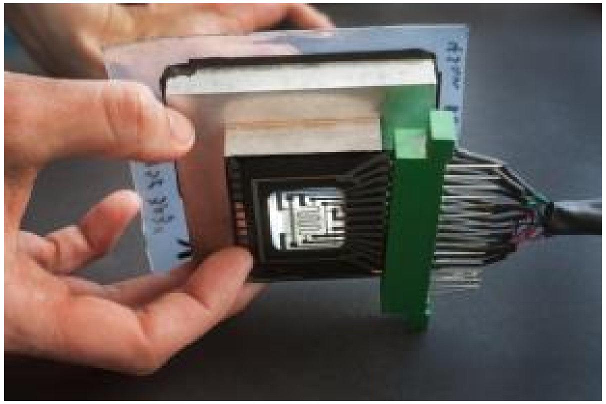


Damp heat chamber for aging samples

Electronics for 128 channel system at Mitsubishi Plastics, Inc.

1. M.O. Reese, A.A. Dameron, and M.D. Kempe, Quantitative Calcium Resistivity Based Method for Accurate and Scalable Water Vapor Transmission Rate Measurement *Rev. Sci. Instr.* 82, 085101 (2011).
2. M.D. Kempe, M.O. Reese, and A.A. Dameron, Evaluation of the Sensitivity Limits of Water Vapor Transmission Rate Measurements Using Electrical Calcium Test, *Rev. Sci. Instr.* 84, 025109 (2013).
3. A.A. Dameron, M.D. Kempe, and M.O. Reese “Internal sensor compensation for increased Ca test sensitivity” *Rev. Sci. Instr.* 85, 075102 (2014)

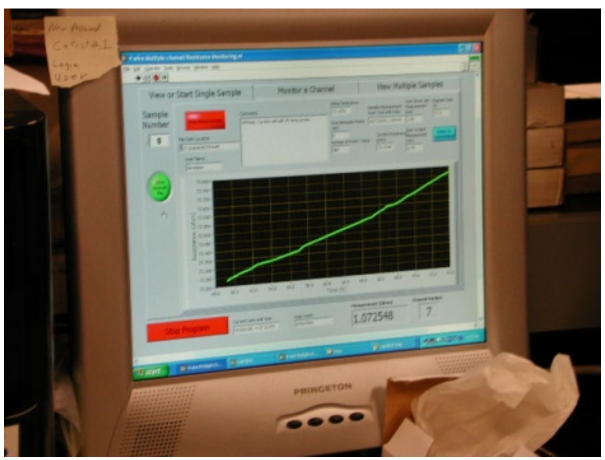
Ca WVTR Measurement



$$Ca + 2\,H_2O \rightarrow Ca(OH)_2 + H_2$$

Conductor → Insulator

$$WVTR = n\delta\rho_{Ca}\left(\frac{l_{eff}}{w}\right)\left(\frac{A_{Ca}}{A_B}\right)\left(\frac{M_w}{M_{Ca}}\right)\left[\frac{d\left(1/R\right)}{dt}\right]$$

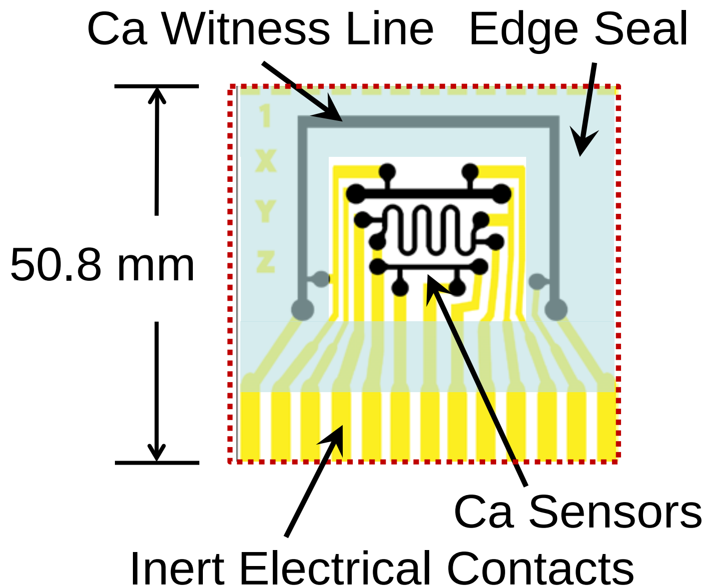


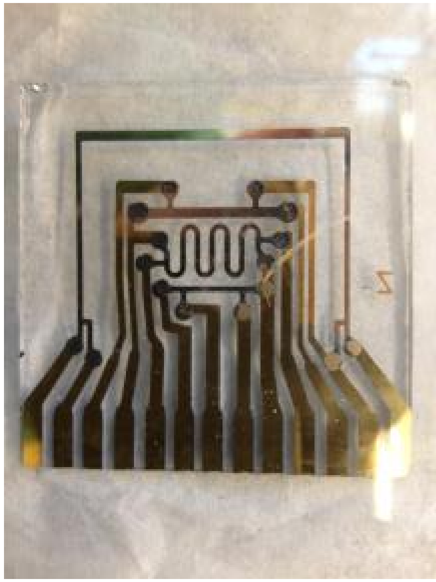
l_{eff} = effective length of calcium
w = width of Calcium
δ = Ca density
ρ_{Ca} = Ca resistivity
A_{Ca} = Exposed Ca Area
A_B = Exposed Barrier Area
n = Reaction ratio of Ca to Permeate.
R = Line Resistance
t = time

M.O. Reese, A.A. Dameron, and M.D. Kempe, Quantitative Calcium Resistivity Based Method for Accurate and Scalable Water Vapor Transmission Rate Measurement *Rev. Sci. Instr.* 82, 085101 (2011).

Test Card

- **Ca Traces are fabricated separate from the barrier film, can be produced in bulk and stored**
- **3 redundant 4-pt measurements of Ca resistance as a function of time**
- **Witness line monitors edge seal integrity and provides internal standard of sensitivity limits**
- **Inert contacts pass signal to the outside of the assembly and fit into standard edge-card connector for ease of connection**





1. M.O. Reese, A.A. Dameron, and M.D. Kempe, Quantitative Calcium Resistivity Based Method for Accurate and Scalable Water Vapor Transmission Rate Measurement *Rev. Sci. Instr.* 82, 085101 (2011).
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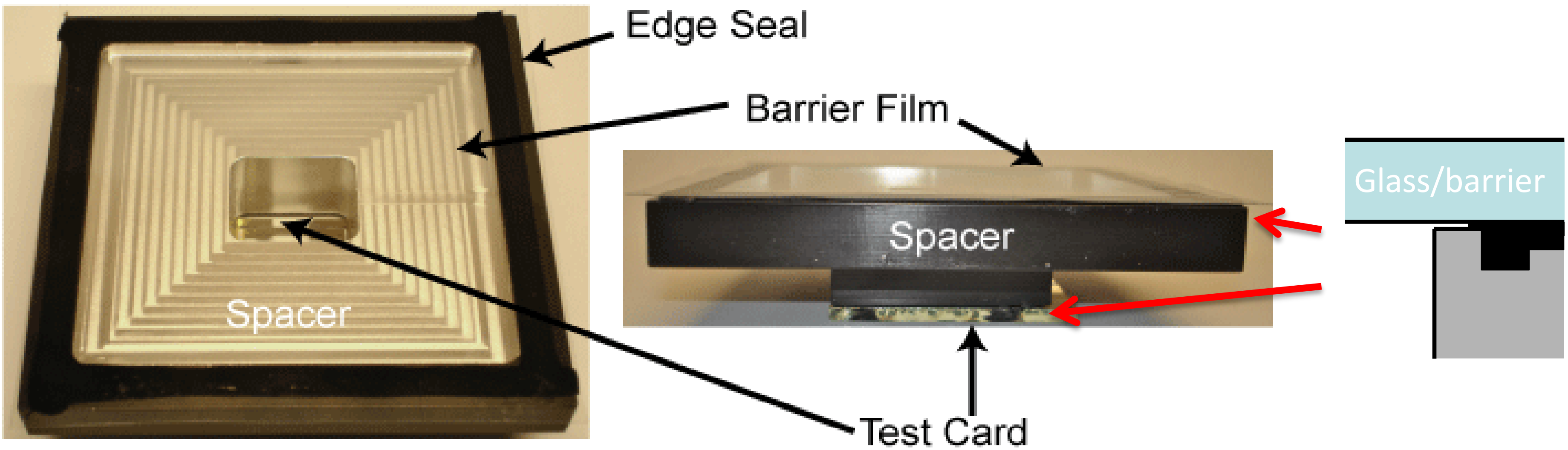
3. A.A. Dameron, M.D. Kempe, and M.O. Reese "Internal sensor compensation for increased Ca test sensitivity" *Rev. Sci. Instr.* 85, 075102 (2014)

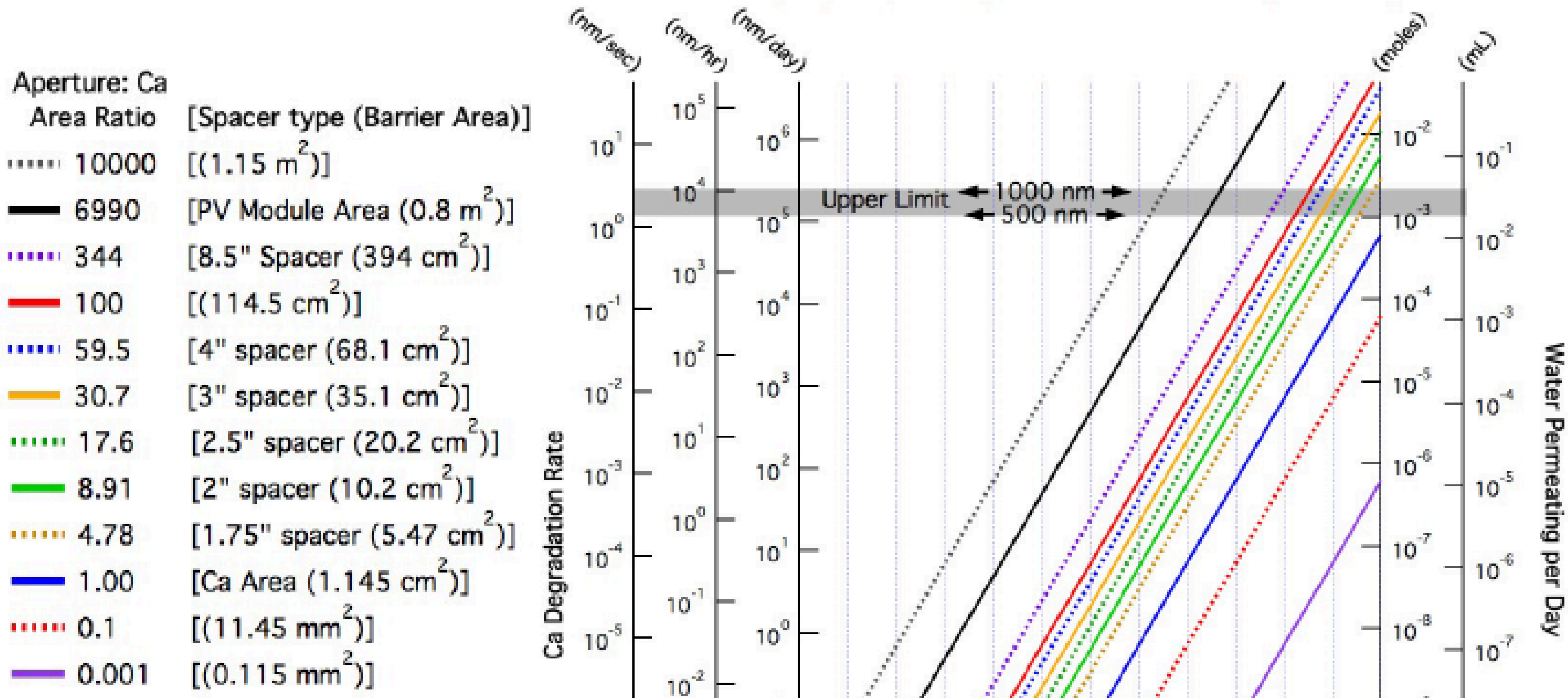
Spacer Advantages



- **Averages over the entire area to provide steady state WVTR**
- **The spacer also allows the Ca Test to be assembled *quickly & easily* with a mechanical press**
- **The sealing surface design allows for *reproducible* areas, and also limits the influence of the edgeseal materials on the measurement**
- **The ratio of apertures *controls the sensitivity range* by adjusting the barrier area relative to the Ca area**

1. M.O. Reese, A.A. Dameron, and M.D. Kempe, Quantitative Calcium Resistivity Based Method for Accurate and Scalable Water Vapor Transmission Rate Measurement *Rev. Sci. Instr.* 82, 085101 (2011).
2. M.D. Kempe, M.O. Reese, and A.A. Dameron, Evaluation of the Sensitivity Limits of Water Vapor Transmission Rate Measurements Using Electrical Calcium Test, *Rev. Sci. Instr.* 84, 025109 (2013).

Spacer Advantage #1: Control Sensitivity

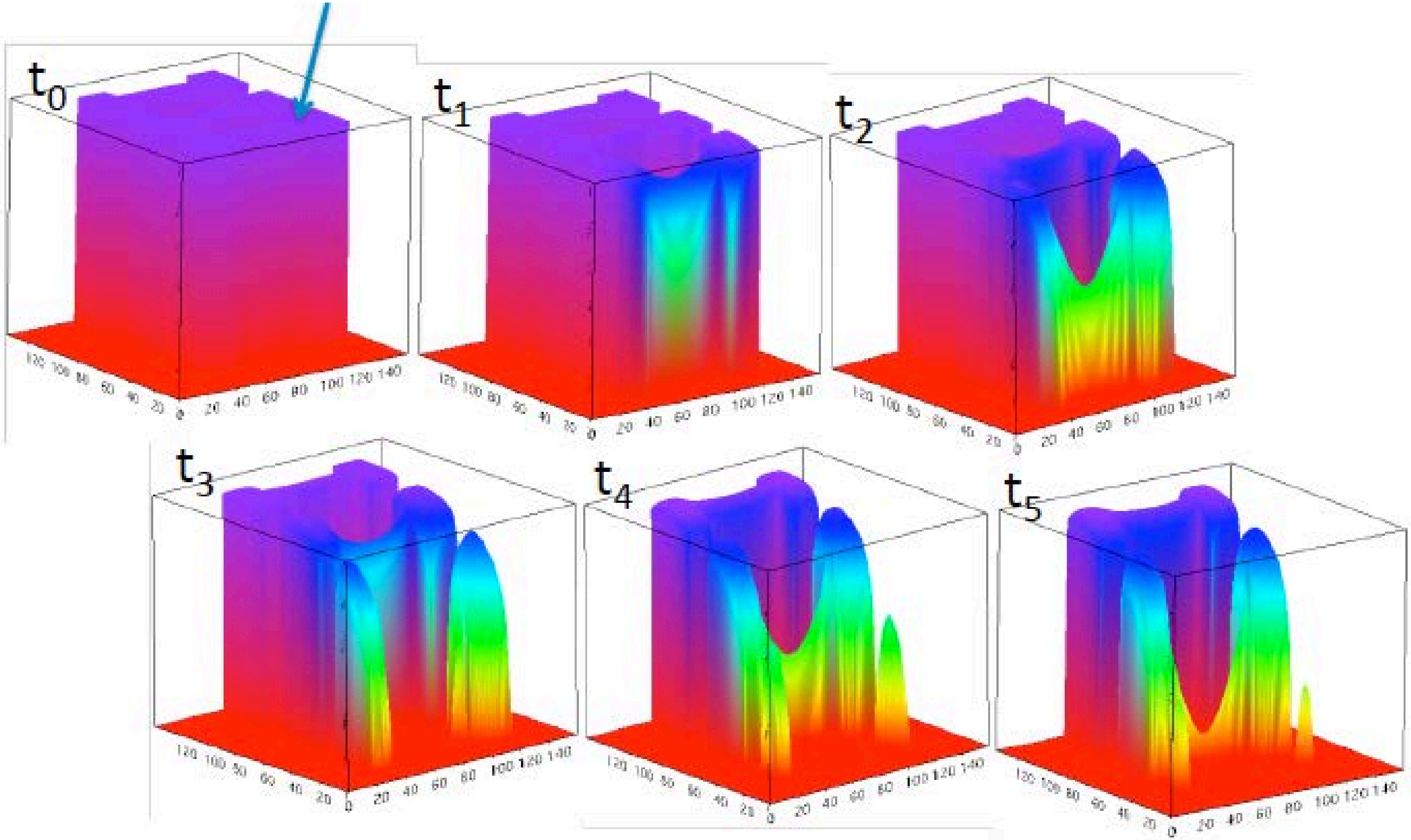


Aperture ratio 1 → 10^{-5} g/m²/day transmitted ~ 1 nm per 1000 hr

A.A. Dameron, M.D. Kempe, and M.O. Reese “Internal sensor compensation for increased Ca test sensitivity” *Rev. Sci. Instr.* 85, 075102 (2014)

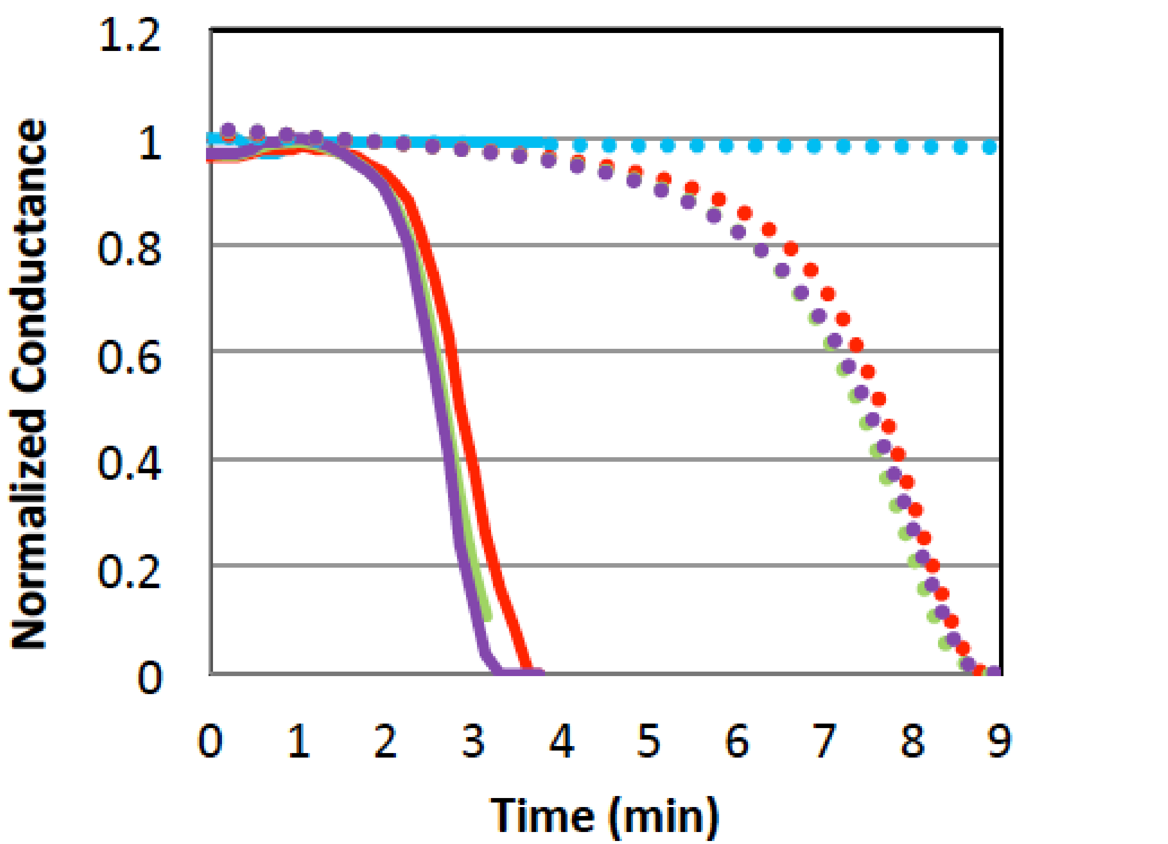
Spacer Advantage #2: Diffusion Compensation

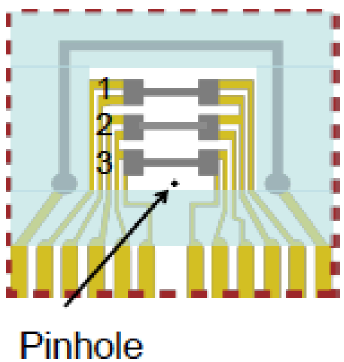
Worst case scenario *(simulation)*: Ca traces are deposited on the barrier but the barrier has a pinhole defect



Resultant measurement is ***NOT*** reflective of the average WVTR

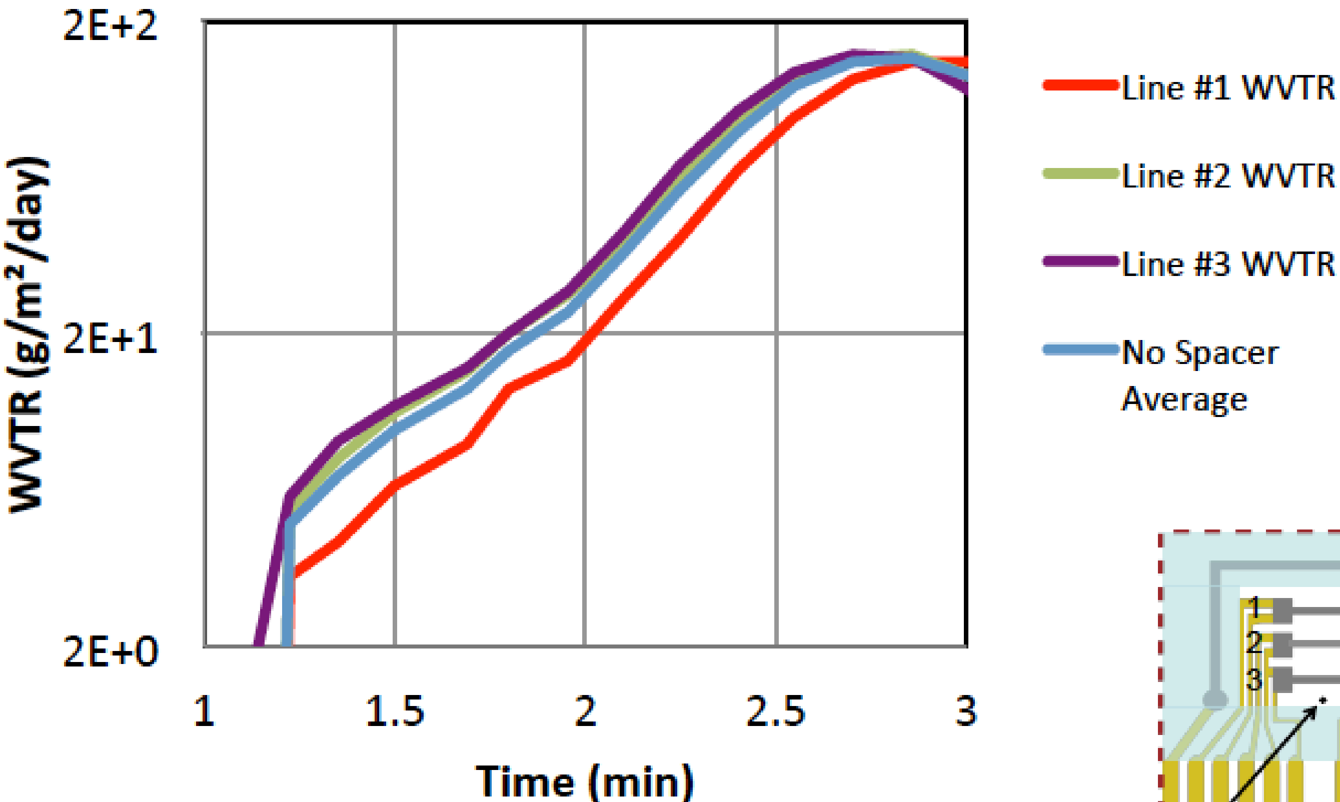
Spacer Advantage #2: Accounting for Defects

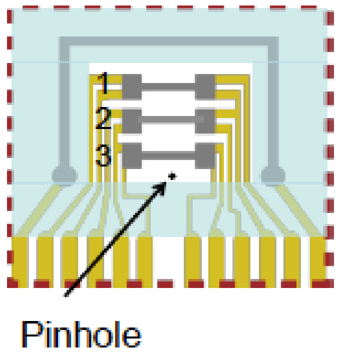




Without a spacer, the trace closest to the pinhole defect produced the highest WVTR

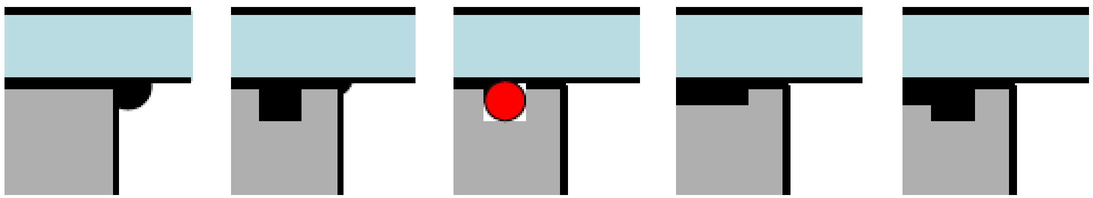
Spacer Advantage #2: Accounting for Defects



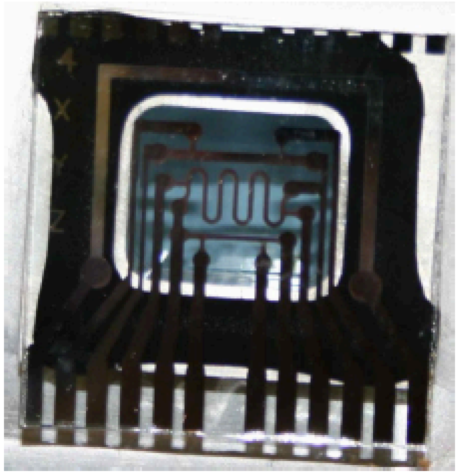


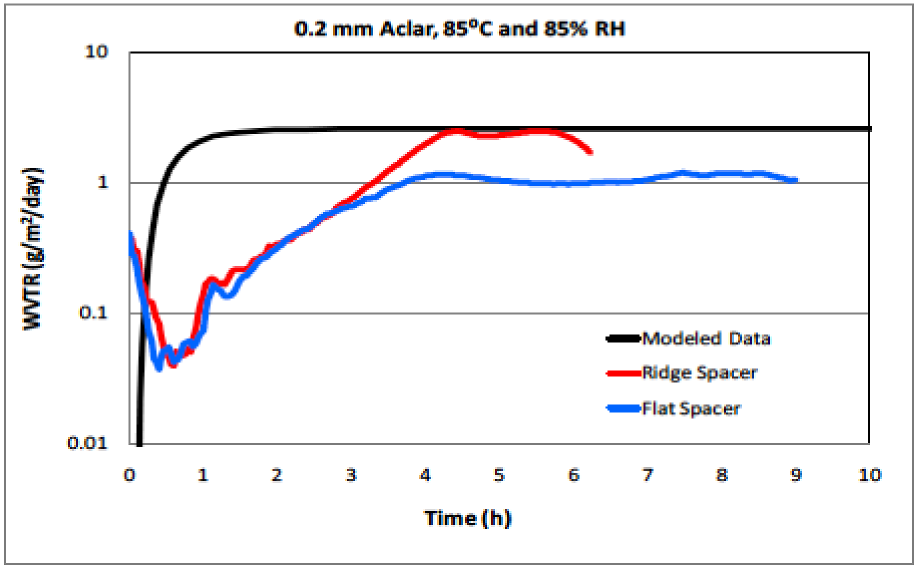
Without a spacer, the trace closest to the pinhole defect produced the highest WVTR.

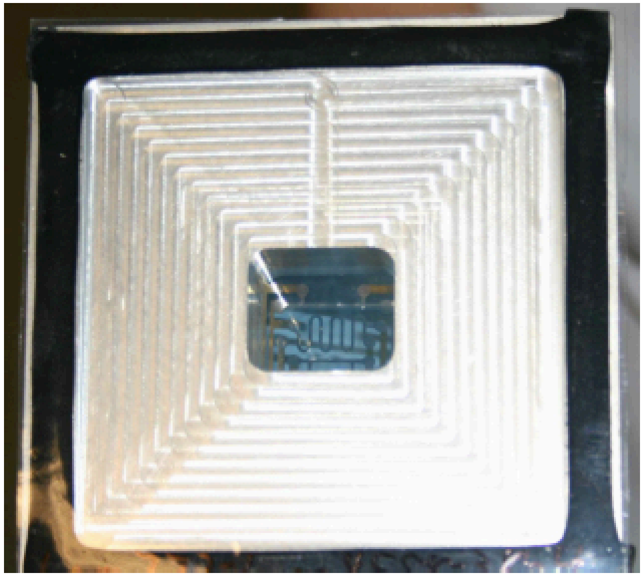
Spacer Advantage #3: Edge Seal Control



(a) Flat (b) Trench (c) "O" Ring (d) Al Ridge (e) Ridge & Trench



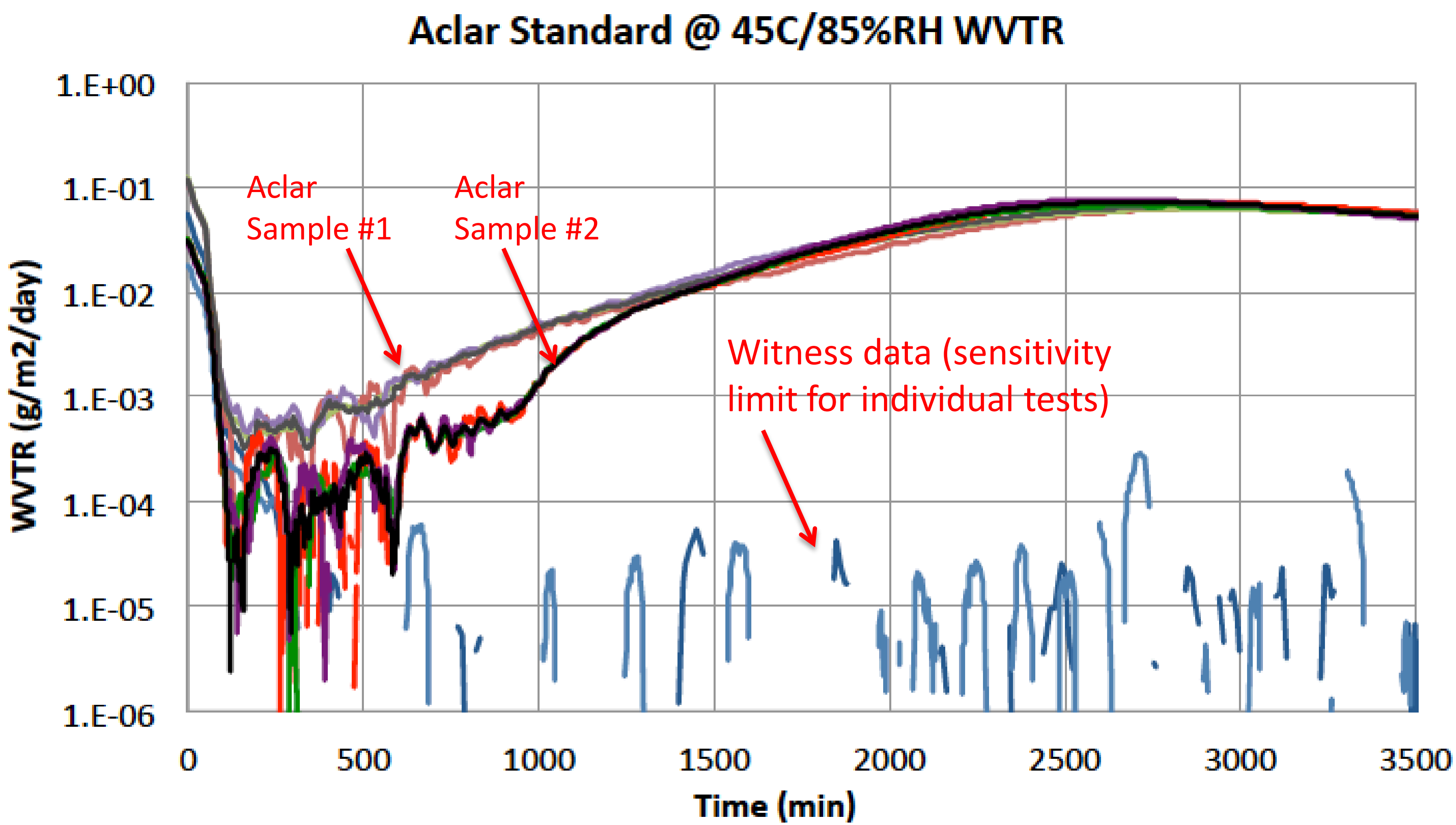




- **Spacer sealing surface design**
  - allows for reproducible testing areas
  - limits the influence of the edgeseal materials on the measurement

1. M.D. Kempe, M.O. Reese, and A.A. Dameron, Evaluation of the Sensitivity Limits of Water Vapor Transmission Rate Measurements Using Electrical Calcium Test, *Rev. Sci. Instr.* 84, 025109 (2013).

Measurement to Measurement Reproducibility



Transients have some irreproducibility, but steady state values should be close

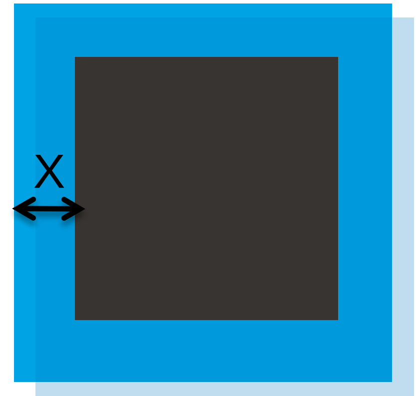
Competing testing methods…

Test Method	Description	Range (g/m²/day)	NREL's Advantage
Cup Test	Scavenger method using gravimetric evaluation	0.1 - 1000	**Range**
Isostatic	Diffusion cell with coulometric moisture sensor or infrared sensor	5×10^{-5} - 200	**Range** **Throughput**
HTO/ Radioactive Tracer	Diffusion cell with detection of water doped with tritium either by ionization chamber or indirectly by hygroscopic salt and scintillation method	10^{-8} - 10	**Ease of Use** **Throughput** **Safety** **Not Commercialized**
Optical Ca Test	Scavenger method monitoring Ca oxide formation optically	10^{-6} - 10	**Ease of Use** **Throughput** **Not Commercialized**
Mass Spectroscopy	Diffusion cell with residual gas analyzer, sometimes paired with programmed valve system to increase sensitivity	10^{-7} - >10	**Ease of Use** **Throughput** **Not Commercialized**
Electrical Ca Test (others)	Scavenger method monitoring Ca oxide formation electrically	10^{-7} - 10	**Ease of Use** **Throughput** **Not Commercialized**
Laser Adsorption Spectroscopy	Diffusion cell with laser diode spectroscopic gas sensor	As low as 10^{-5}	**Range** **Throughput**

M.D. Kempe, M.O. Reese, and A.A. Dameron, Evaluation of the Sensitivity Limits of Water Vapor Transmission Rate Measurements Using Electrical Calcium Test, *Rev. Sci. Instr.* 84, 025109 (2013).

Edge Seal Evaluation

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

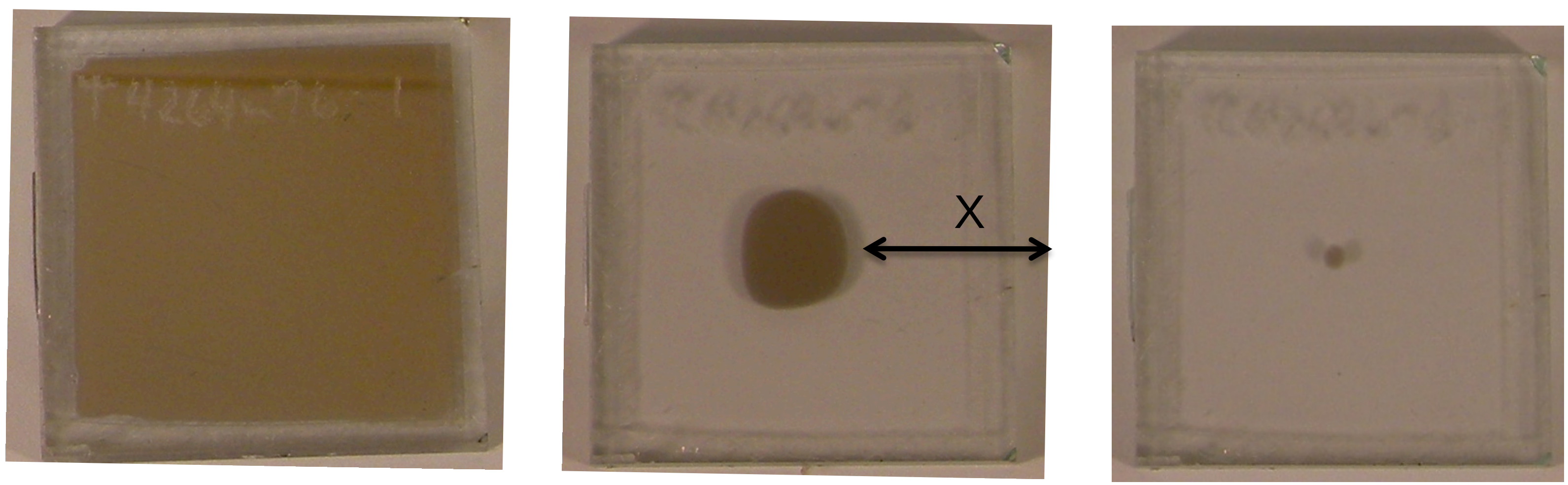


Ca turns transparent appearing to shrink toward center

$$\boxed{X = K\sqrt{t}}$$

PDMS

85C/ 85 %RH



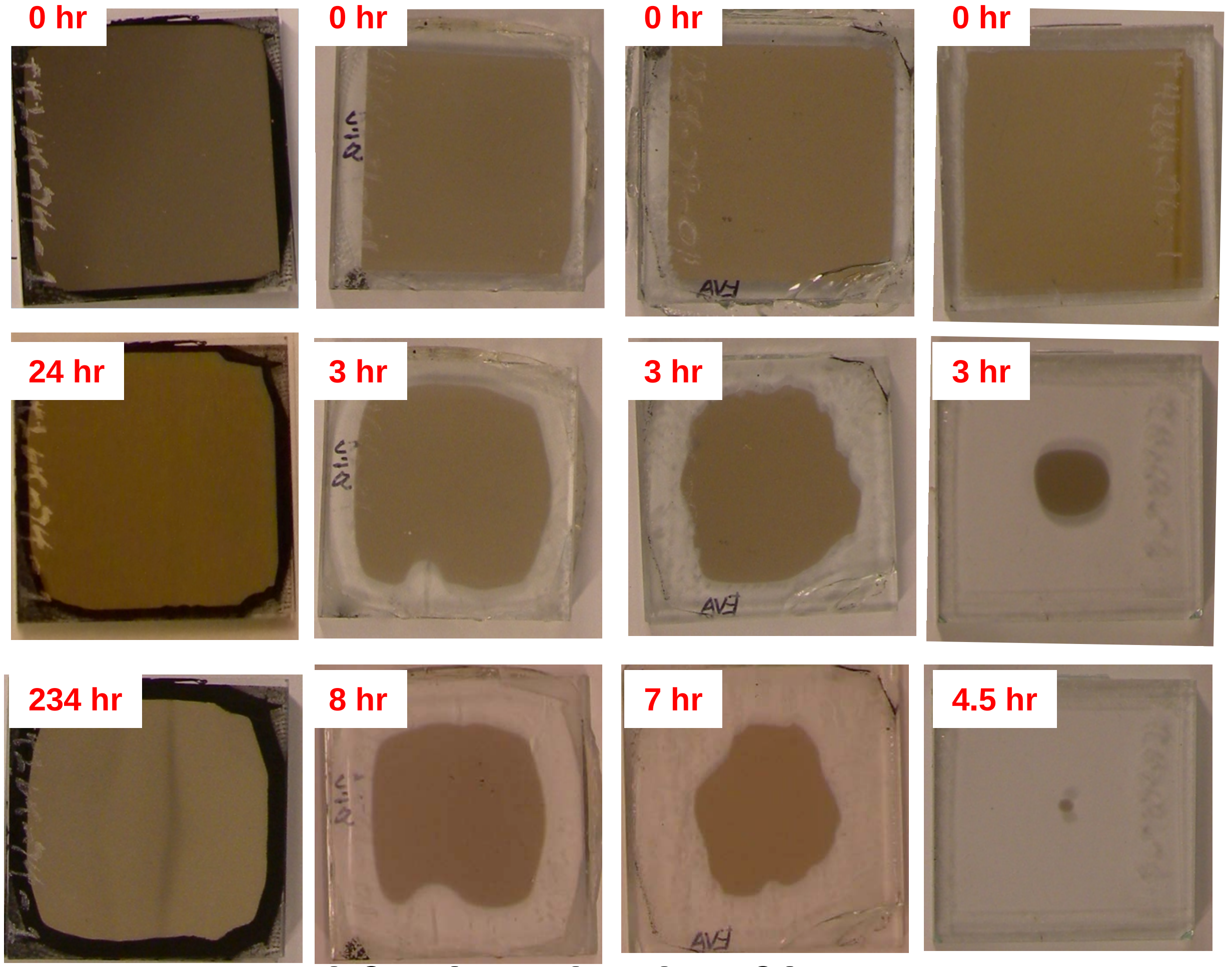
0 h **3 h** **4.5 h**

M.D. Kempe, A.A. Dameron, and **M.O. Reese**, “Evaluation of moisture ingress from the perimeter of photovoltaic modules” Prog. Photovolt: Res. Appl. 22, 1159 (2014). doi: 10.1002/pip.2374

Typical Edgeseal Results

Desiccant-filled Polyisobutylene | PVB | EVA | PDMS

Increasing Time



We tested for hundreds of hours….

M.D. Kempe, A.A. Dameron, and **M.O. Reese**, "Evaluation of moisture ingress from the perimeter of photovoltaic modules" Prog. Photovolt: Res. Appl. 22, 1159 (2014). doi: 10.1002/pip.2374

Desiccant Filled PIB Edgeseal

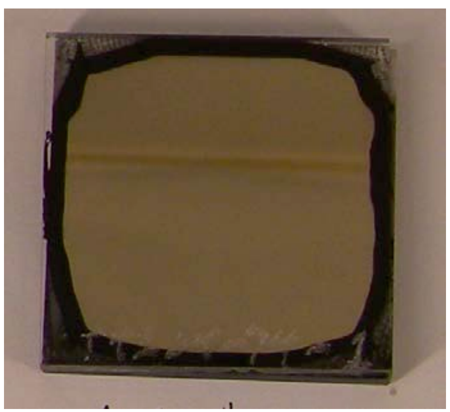
0 hr

210 hr

282 hr

575 hr

We've tested for thousands of hours, but sometimes there are interactions….



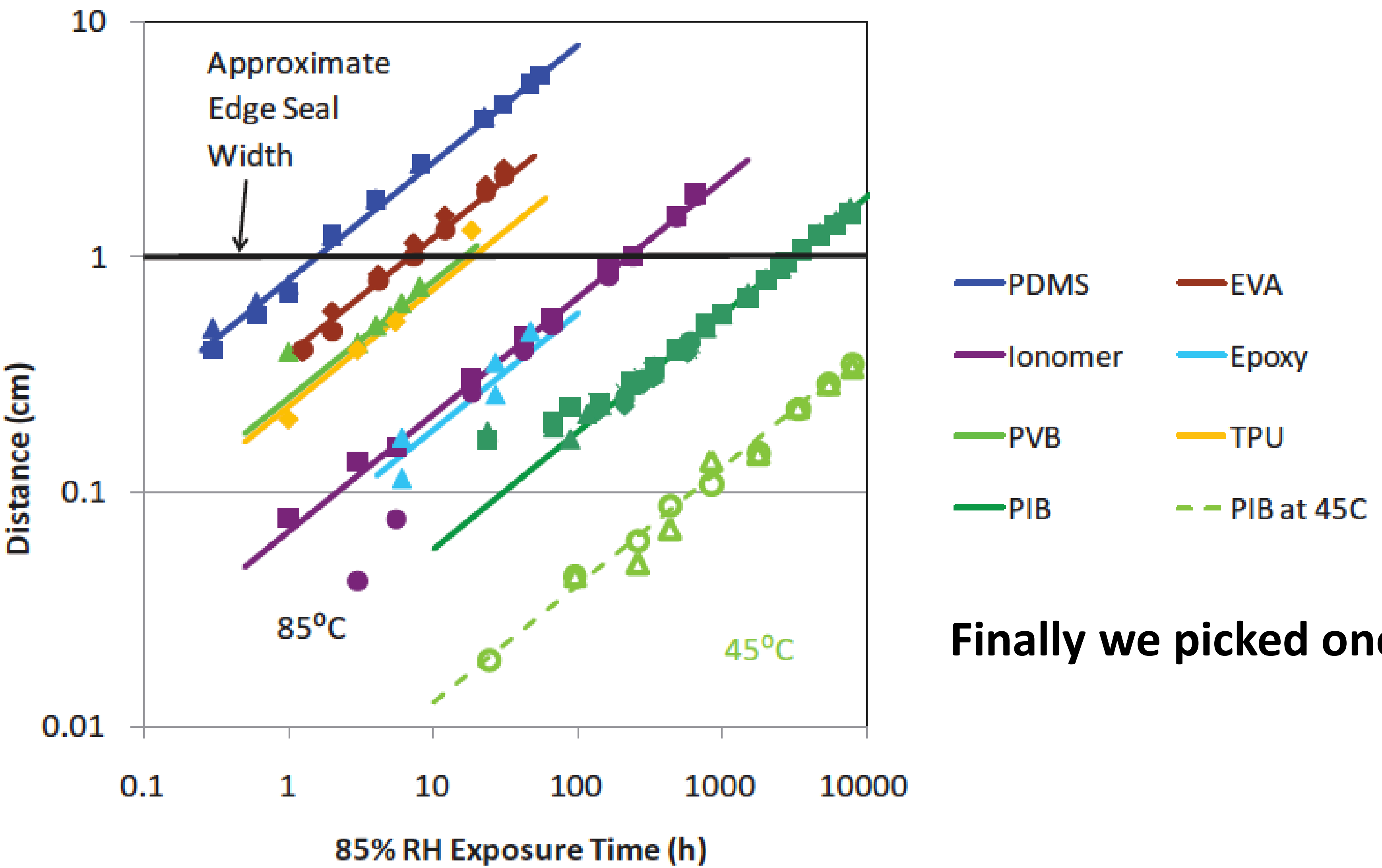
115 h

1488 h

3509 h

M.D. Kempe, A.A. Dameron, and **M.O. Reese**, "Evaluation of moisture ingress from the perimeter of photovoltaic modules" Prog. Photovolt: Res. Appl. 22, 1159 (2014). doi: 10.1002/pip.2374

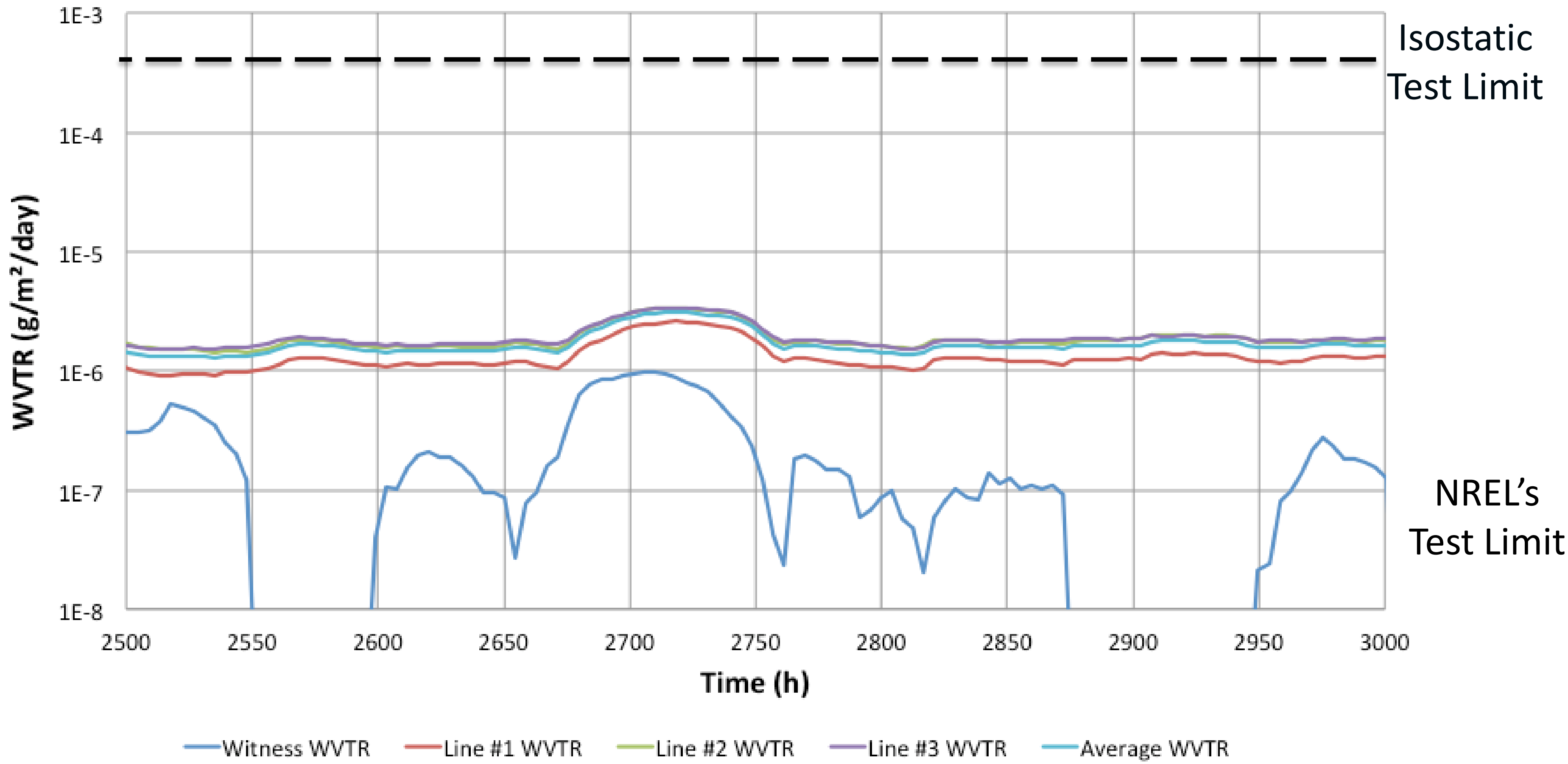
Relative Comparison of Materials



Finally we picked one!

M.O. Reese, A.A. Dameron, and M.D. Kempe, Quantitative Calcium Resistivity Based Method for Accurate and Scalable Water Vapor Transmission Rate Measurement *Rev. Sci. Instr.* 82, 085101 (2011).

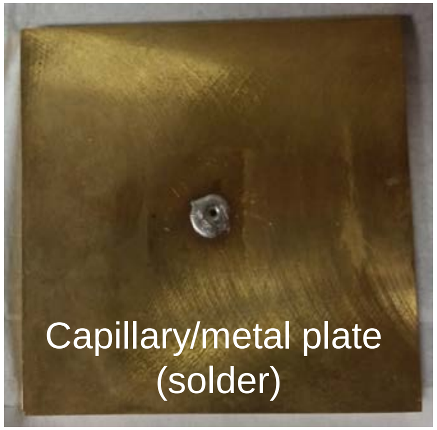
Measured NREL e-Ca Test Data

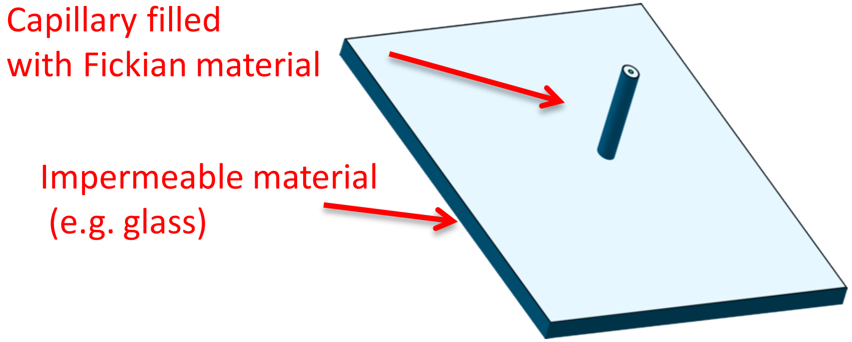


Actual measured data from a barrier film provided by a commercial partner

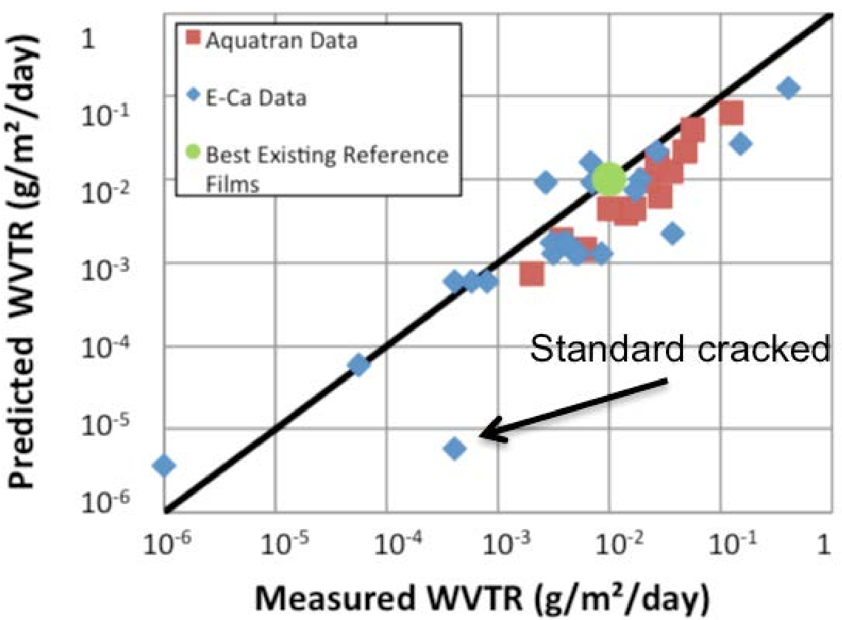
Development of WVTR Standards

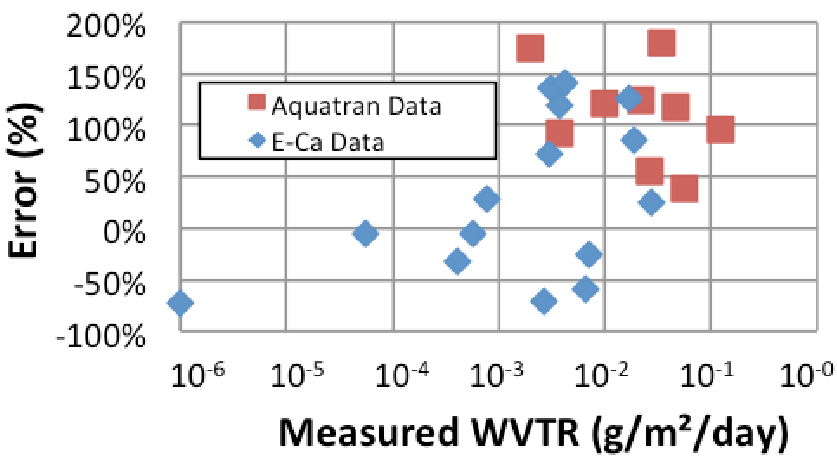
- **Meaningful moisture vapor barriers for PV require WVTR <10^{-4} g/m^2/day**
- **Reasonable thickness polymer films can only get to ~10^{-2} g/m^2/day**
- **Standards do not exist below ~10^{-2} g/m^2/day**
- **Goal: Generate *WVTR Standards* from 10^{-2} to 10^{-7} g/m^2/day**





Development of WVTR Standards





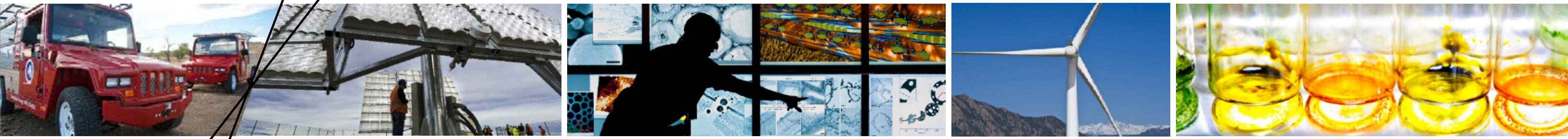
- **We are working on reducing errors due to**
  - Delamination
  - Cure inhibition
  - Residual strain in polymer chains
- **Most people only trust WVTR to an order of magnitude; we hope to reduce errors to <20%**

Acknowledgements

- We (Matthew Reese, Arrelaine Dameron, and Michael Kempe) would like to thank all of the people who have helped us over the years in the development of this measuring technique for high barrier transparent films.
- Thomas Moricone, Dylan Nobles, Byron McDanold, Talysa R. Klein, Joshua Martin, Trevor Lockman, Dierdre Johnson.

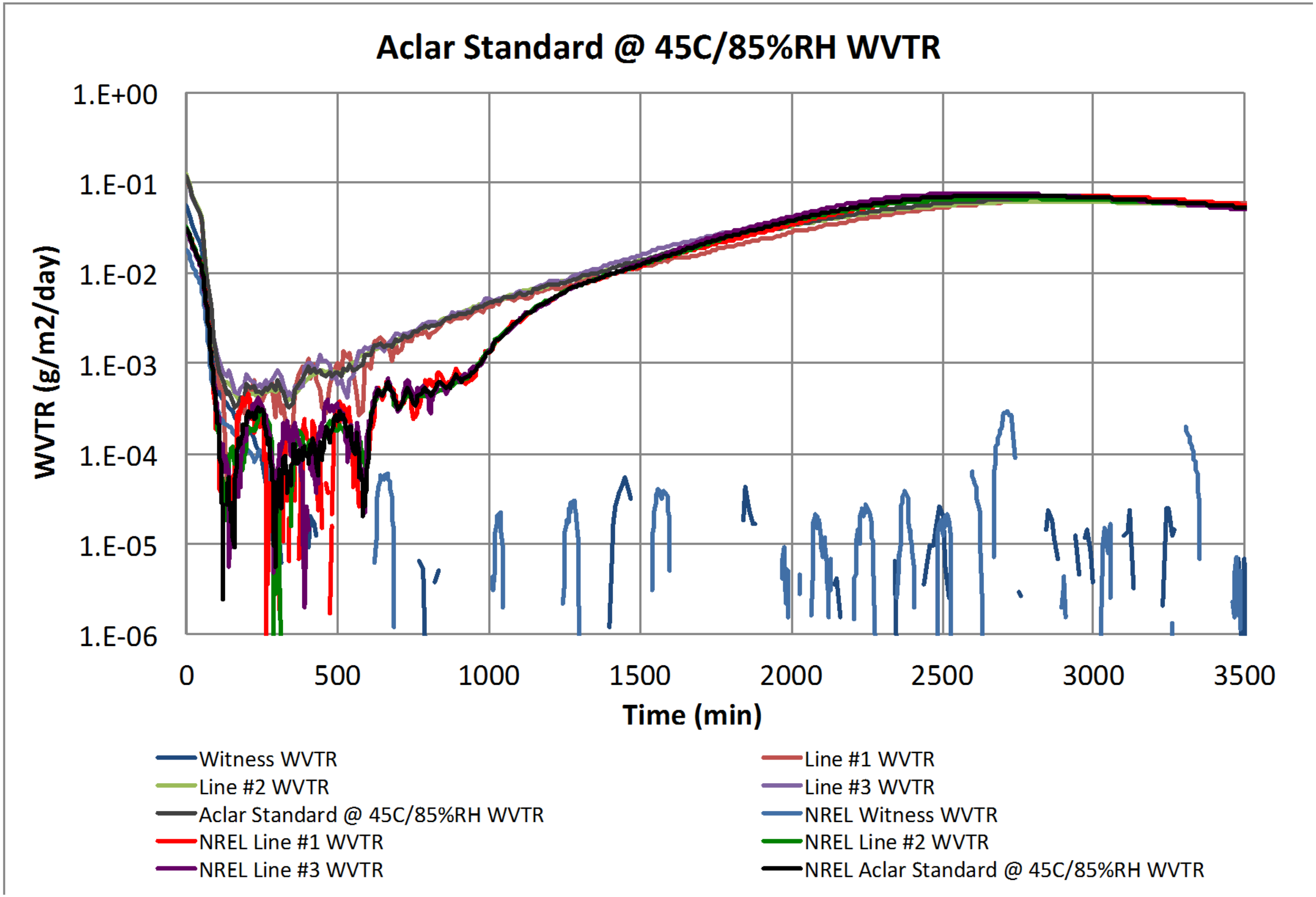
BAPVC BAY AREA PHOTOVOLTAIC CONSORTIUM

DuraMAT Durable Module Materials Consortium



Sample Section Divider

Device to Device reproducibility



WVTR Equation

Reaction Ratio:

$Ca + 2H_2O(g) \rightarrow Ca(OH)_2 + H_2$

n=2

Ca Density:

1.55 g/cm^3

Ratio of Apertures

Measured Resistance

$$WVTR = n\delta\rho_{Ca}\left(\frac{l_{eff}}{w}\right)\left(\frac{A_{Ca}}{A_B}\right)\left(\frac{M_w}{M_{Ca}}\right)\left[\frac{d\left(\frac{1}{R}\right)}{dt}\right]$$

Ca Resistivity:

4.02×10^{-6} ($\Omega\cdot$cm) at 23^{o}C

Trace Dimensions

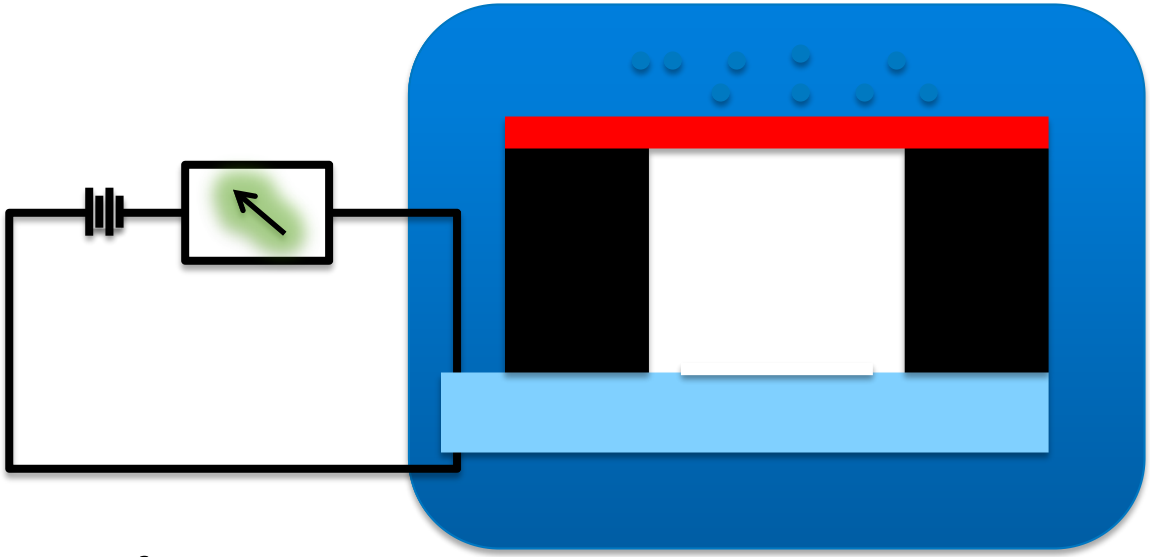
Ratio of Molecular Weights

Time

$$R_0 = \frac{R}{1+\alpha(T-T_o)}$$

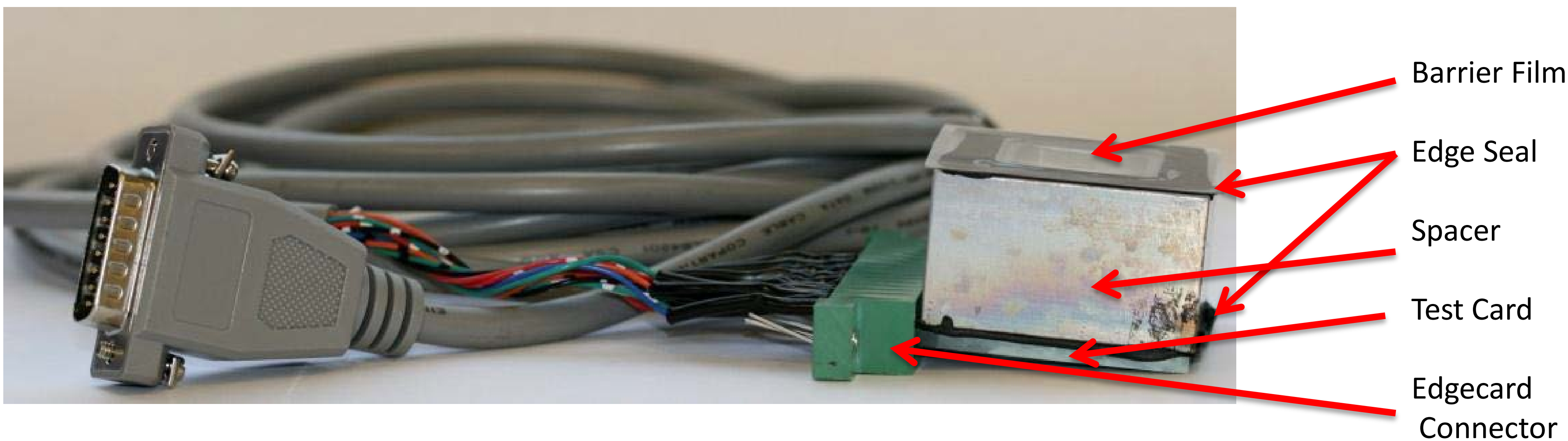
We measure the resistance with respect to time to calculate the WVTR.

NREL’s e-Ca Test



$Ca + 2H_2O(g) \rightarrow Ca(OH)_2 + H_2$

Ca transforms from opaque, conductive metal to transparent, resistive oxide upon exposure to water



Things to include

- **Edge ingress**
  - Epoxy, brittle & can react
- **Degassing residual moisture**
- **Timescales for long measurements**
- **Low resistance measurement**
  - Proper 4-wire measurement
  - Getting correct ranges
  - Sensitivity with increased resistance
  - Non-bulk R
- **Pinhole detection**
- **Effect of large area unpatterned Ca layer**
- **Non uniform Ca consumption**
  - Pinholes
  - Uniform degradation assumption vs irregular – Nissen citation + otehr
- **Corrosion at Ca/electrode interface**
  - Intermetallic formation
  - Galvanic corrosion
- **Interaction with Glass**