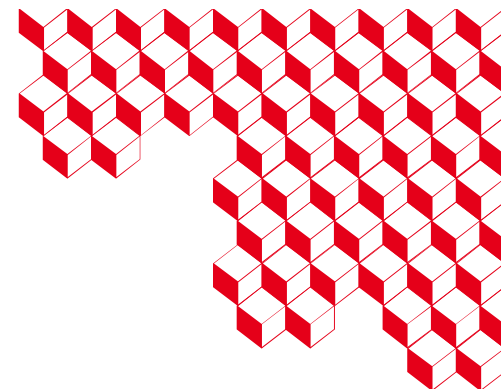




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## **Perovskite photovoltaic: Extrinsic stability and Encapsulation challenge**

[stephane.cros@cea.fr](mailto:stephane.cros@cea.fr)



14th SOPHIA PV-Module Reliability Workshop  
Hasselt University (Belgium), 25.-26.04.2024

# outline



- Who we are
- Extrinsic stability: encapsulation need
- Different encapsulation methods
- Gas barrier measurements in CEA
- Joint HZB/CEA study about lamination of PVK device
- Joint Arkema/CEA study about gas barrier adhesives
- CEA study about the influence of buffer layers

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Defence Security	Nuclear Energy	Research & Technology	 4 500 employees 550 M€ budget 500 priority patents filed / year 50 spin-off companies
Defence Applications Division	Nuclear Energy Division	Technological Research Division	
			

**Fundamental Research**  
Material Science Division / Life Science Division



	<b>16 000 employees in 10 research centers</b> <b>4 B€ annual budget</b> <b>580 priority patents filed / year</b> <b>120 new high tech companies created since 1984</b>
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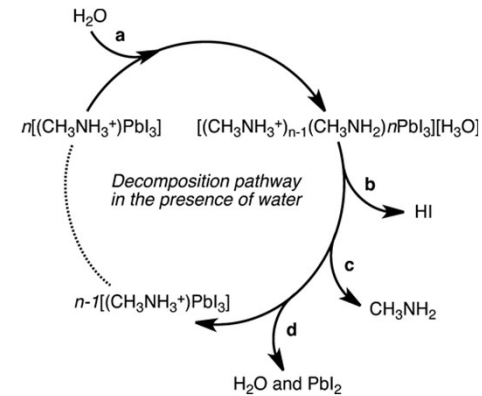
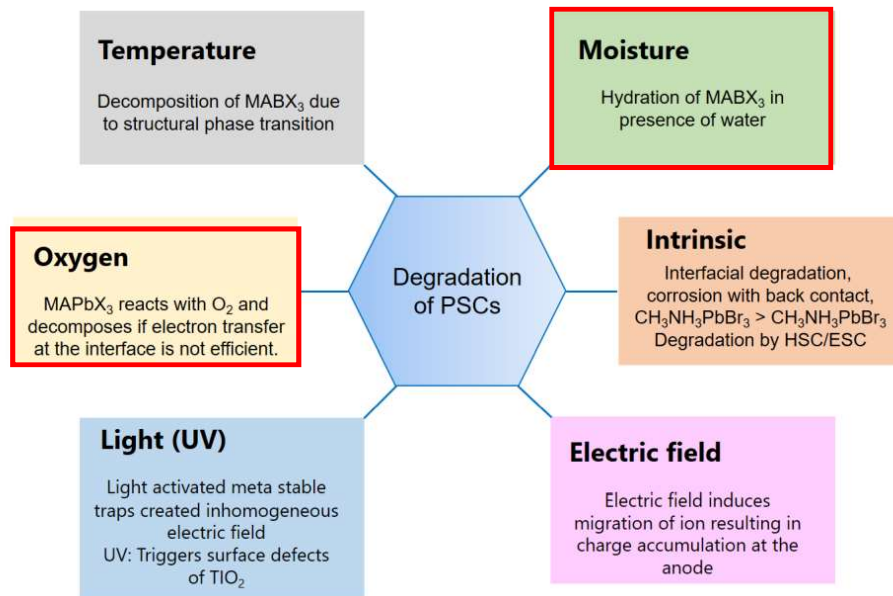


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# Extrinsic degradation



Bakr, Z. & al. *Nano Energy* 2017, 34, 271–305.  
 Frost, J. M &al. *Solar Cells. Nano Lett.* 2014, 14 (5), 2584–2590

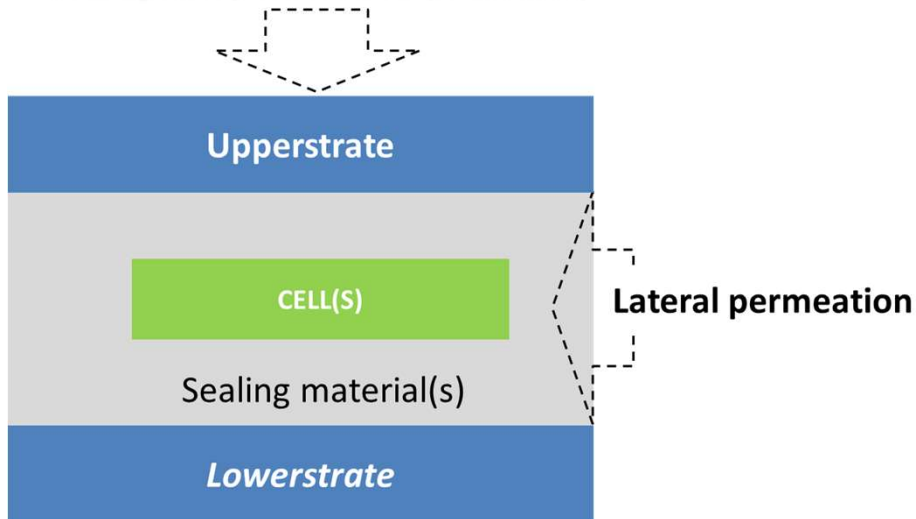
So far, Perovskite based solar cells need a strong encapsulation to prevent moisture/oxygen ingress

This is key issue for long lifetime achievement and cost

# Extrinsic stability/Encapsulation



Orthogonal permeation (if flexible)



- **Gas barrier requirements are high** and will depend of stack resistance versus diffusing gases and lifetime targets
- The encapsulation process can lead to performance losses because of the **thermo-mechanical resistance** of the PVK cell (degradation, delamination)
- Encapsulation procedures and materials need to be adapted **with a controlled cost**
- A lot of device configuration are developed (rigid, flexible, tandem..) but we can highlight main features:
  - sheet to sheet encapsulation using hot vacuum lamination **OR** roll to roll lamination.
  - Rigid OR flexible devices
  - Possible additional thin film encapsulation

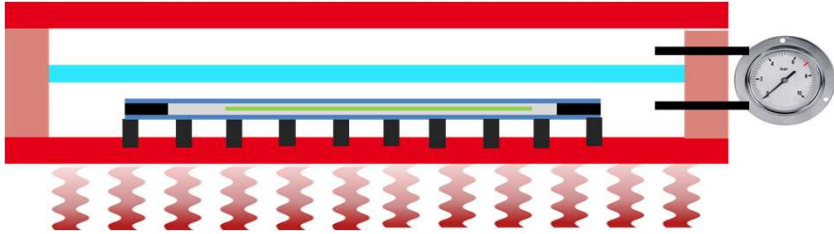
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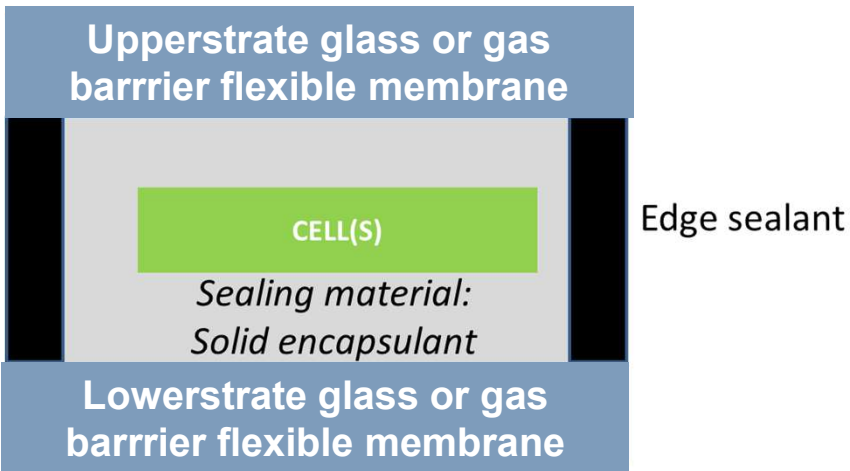
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# Sheet to sheet lamination



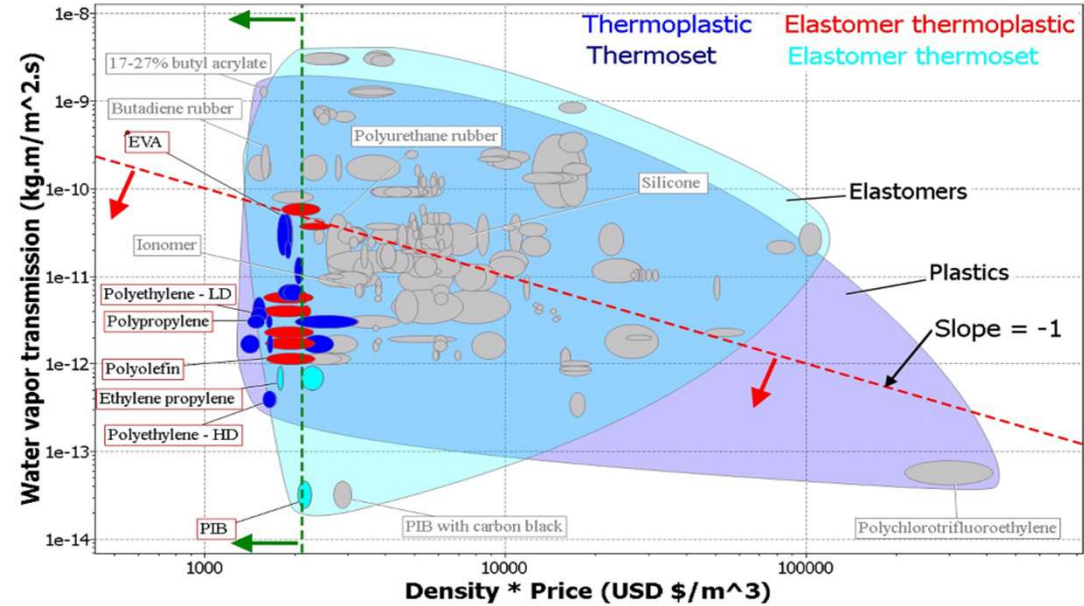
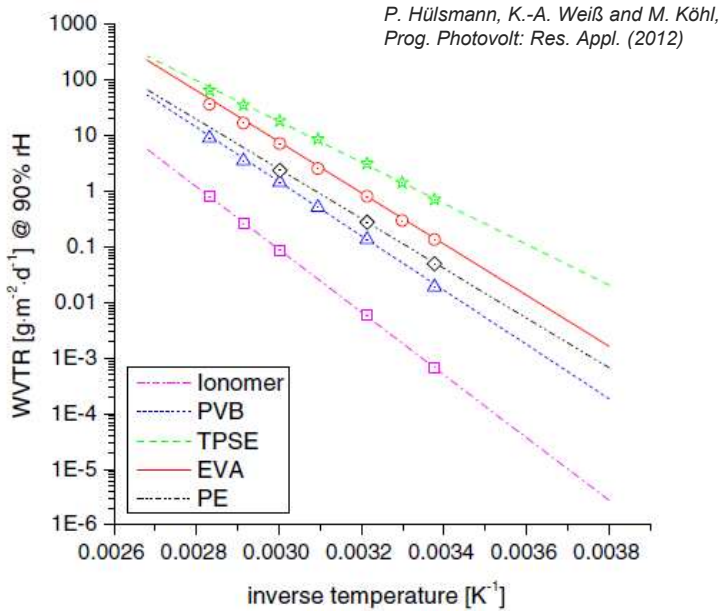
- The process will combine heating and vacuum to seal rigid or flexible covers to the device
- PVK technologies: need for optimization of lamination procedures (temperature resistance, pressure)
- Many sealing materials (providers) can be considered. The selection will depend on **thermo-mechanical profile and gas barrier properties**
- The use of additional edges sealant (generally opaque) reduce the water vapour side permeation



# Sheet to sheet lamination

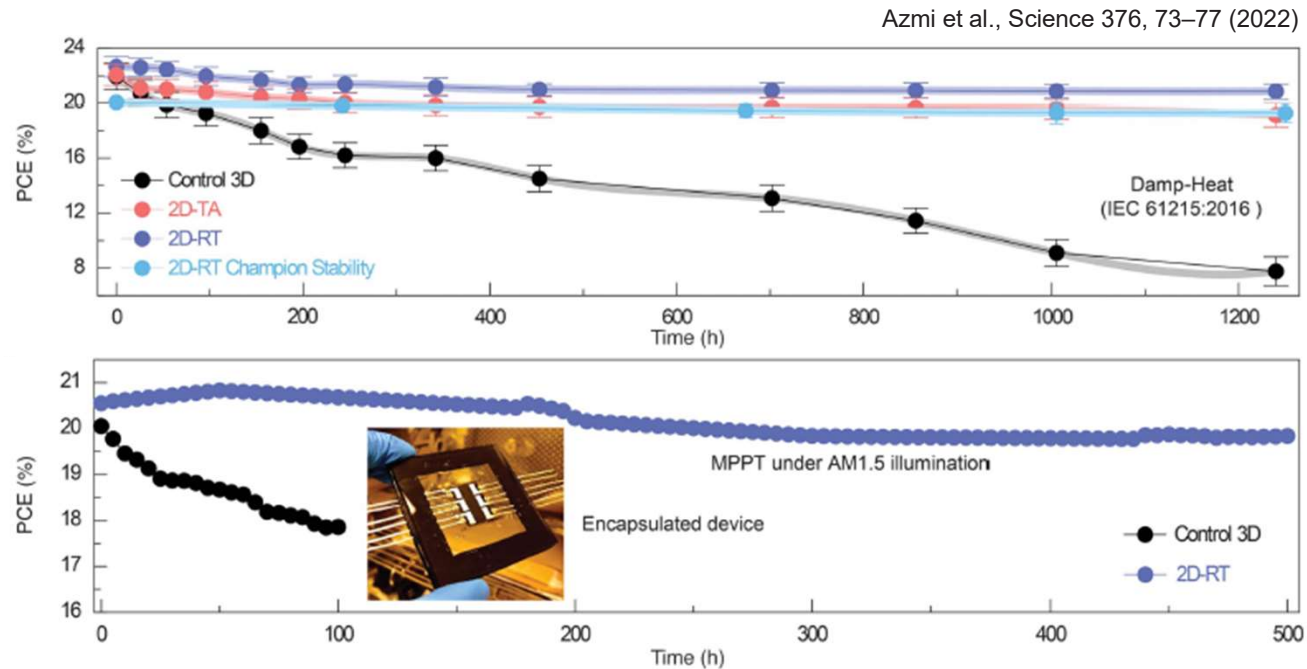


Shimpi&al.Sol. Energy 2019, 187, 226–232.  
<https://doi.org/10.1016/j.solener.2019.04.095>.



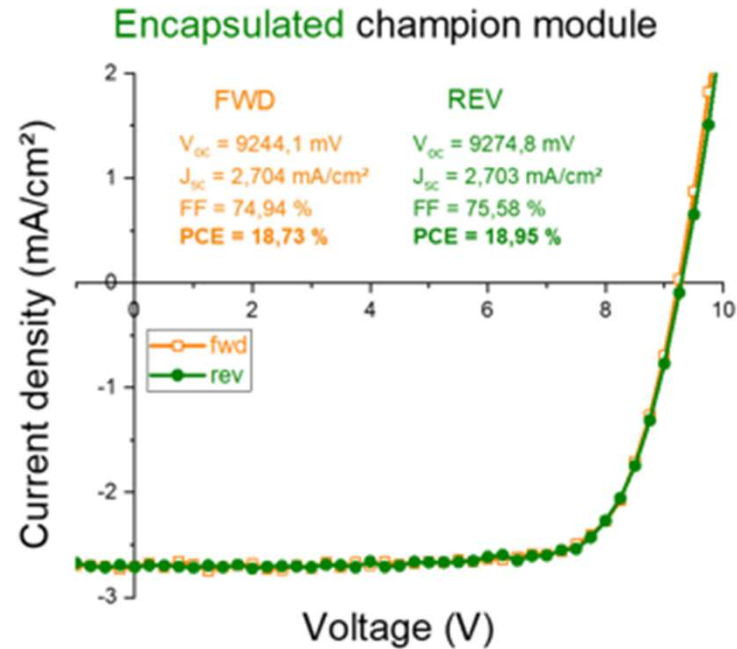
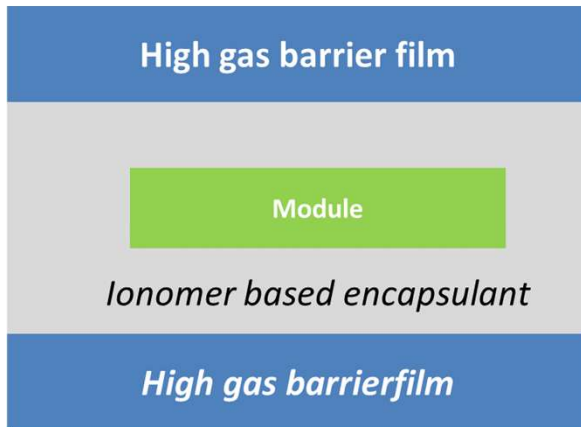
- The gas barrier characteristics of the common EVA is poor, plus by products
- Process with  $T^\circ (\geq 130^\circ\text{C})$  can be complicated for many PVK based technologies
- The impact of the pressure can be not negligible
- Damp heat aging ( $85^\circ\text{C}$ , 85%RH) and thermal cycling are the main standard regarding encapsulation assessment

# Sheet to sheet lamination



- Glass/glass encapsulation using hot vacuum lamination, encapsulant and butyl rubber **edge sealant**
- Damp heat aging at 85°C/85%RH
- The degradation kinetic will depend on intrinsic resistance of the stack and/or PVK absorber (passivation)
- Degradation mechanisms are complex and could also occurs at the interfaces, or related to temperature
- The check of **the intrinsic stability (temperature, light) of encapsulated PVK device is crucial**

# Sheet to sheet lamination

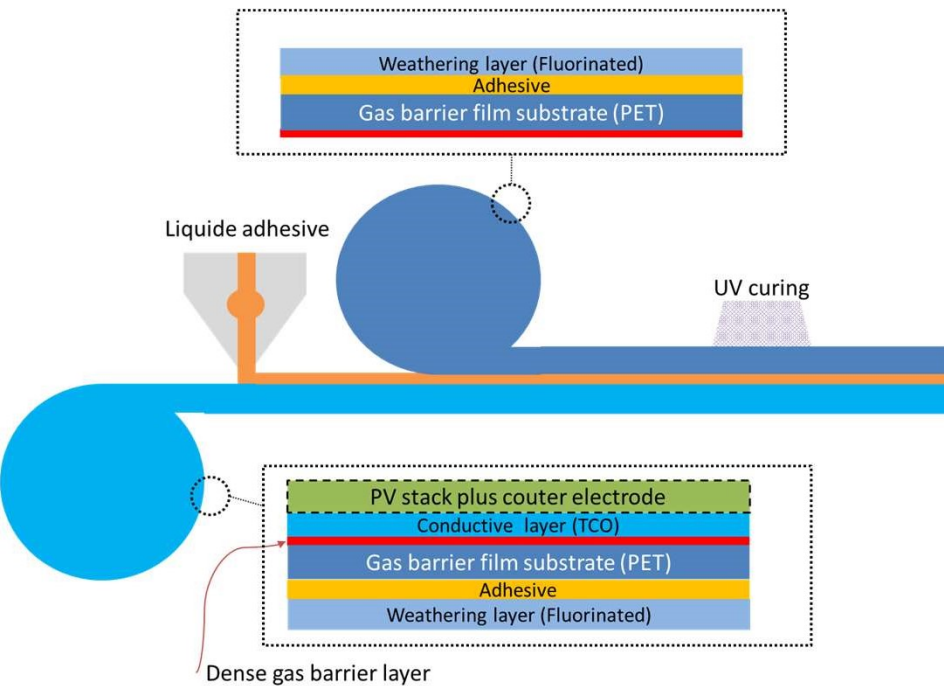


CEA achievement in Apolo Eu project:

- Hot vacuum encapsulation procedure at 130°C using ionomer sealant
- Flexible covers (commercial) with high gas barrier characteristics
- NO losses after encapsulation using CEA mini modules (11cm<sup>2</sup>, NIP single junction)
- T90 at 400 hours in damp heat conditions (85°C, 85%RH)



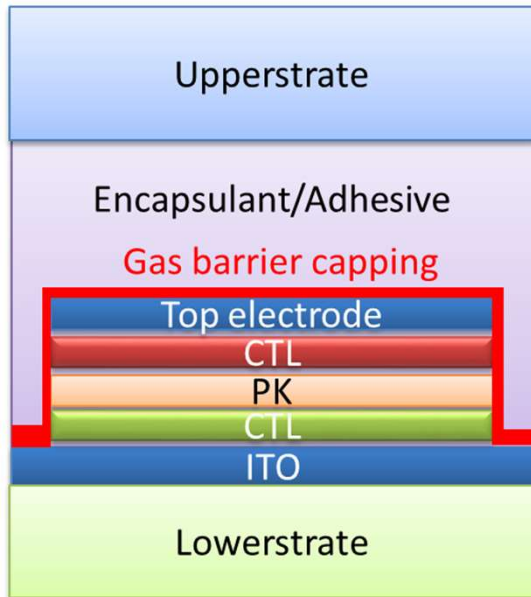
# Roll to roll encapsulation



- Use of **flexible gas barrier covers** (commercial) with low WVTR ( $10^{-3}/10^{-4} \text{ g.m}^{-2}\text{d}^{-1}$ )
- The front encapsulation can be included in the transparent conductive film (TCF) used as a substrate of the active layers
- The TCO scribing process need to be optimized to not damage the barrier layers (can be replaced by printed electrodes)
- **Gas barrier properties are required for the adhesive** because the use of edge sealant is more complicated (/sheet to sheet) (in the range  $1- 2\text{g.mm. m}^{-2}\text{d}^{-1}$ )
- **UV polymerization/curing** is often used. Need to be polymerized/cured in **1-2 minutes** (or use of pressure sensitive adhesives)
- Adhesives based on acrylic or epoxy chemistry are the most employed
- The radius of curvature of the encapsulated device is related to the nature of materials and the thickness



# Thin film encapsulation



technology	widely used materials	WVTR range 38°C / 90% r.h. [g/(m <sup>2</sup> d)]	typical layer thickness [nm]	productivity (web speed or deposition rate) [m/min]	references
thermal or electron beam evaporation	AlO <sub>x</sub> , SiO <sub>x</sub>	> 0.5 g/(m <sup>2</sup> d) on PET	5 ... 20	≈ 600	[13-15]
(reactive) sputtering	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , Zn <sub>2</sub> SnO <sub>4</sub> ,	0.01 on PET 0.001 on PEN	40 ... 200	≈ 1	[16-19]
plasma assisted chemical vapor deposition (PECVD)	SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> , SiO <sub>x</sub> N <sub>y</sub> ,	< 10 <sup>-3</sup> g/(m <sup>2</sup> d) ... 1 g/(m <sup>2</sup> d)	100 ... 1000	≈ 1 ... 0.1	[20-22]
atomic layer deposition (ALD)	Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	< 10 <sup>-3</sup> g/(m <sup>2</sup> d)	10 ... 25	0.1 nm/cycle	[9, 23-26]

*John Fahlteich & al. The Role of Defects in Single- and Multi- Layer Barriers for Flexible Electronics, Fall 2014 SVC Bulletin,*

- Gas barrier layer capping can improve the resistance against diffusing gases
- The coating technology will lead gas barrier performances and compatibility with the device
- ALD and PEVCD allow the deposition of high quality layers
- The throughput of the process remains a challenge regarding the cost of the final module



## outline

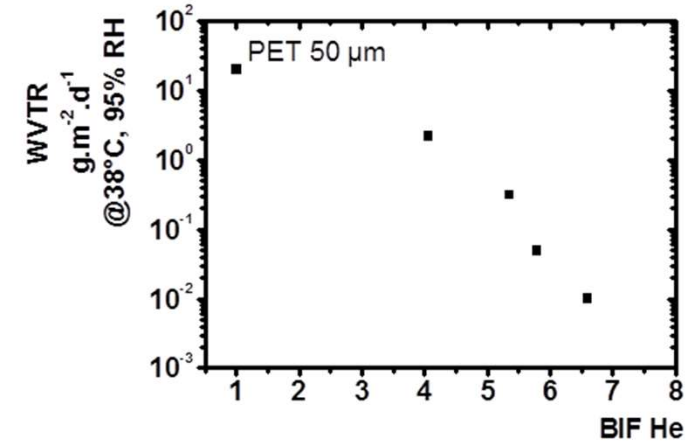
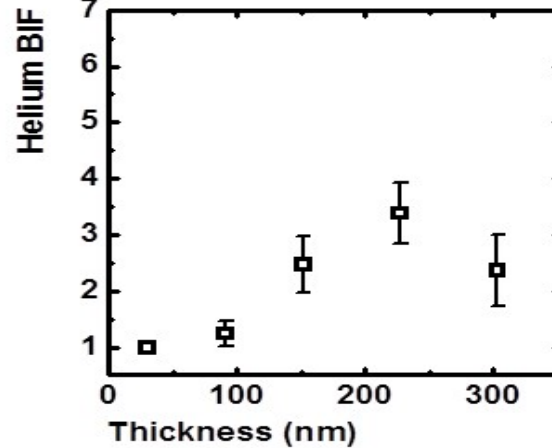
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# Orthogonal Permeation measurement



A.Morlier et al./SolarEnergyMaterials&SolarCells115(2013) 93–99



VinciTechnologies  
QHV-4



- We developed fast quality control procedure to develop rapidly thin gas barrier coating
- The technology based on helium permeation and mass spectrometry allow to measure 1 sample every 1 or 2 hours against several days or week for water vapour permeation measurement
- The same technology (mass spectrometry) allow to measure ultra low WVTR (gas barrier film)
- Helium quality control allow us to assesses rapidly the resistance of the gas barrier performances versus different stress (T°, humidity, light, bending..)

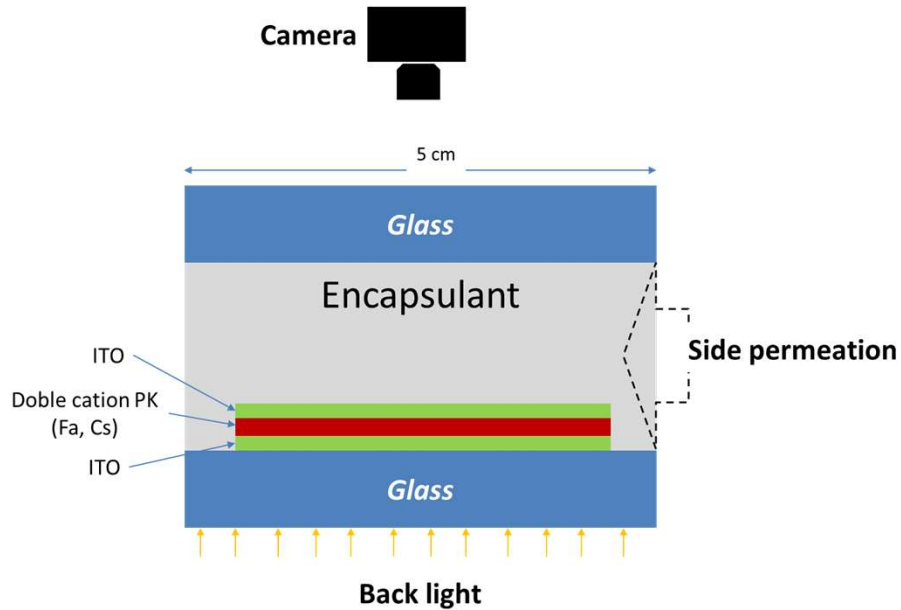




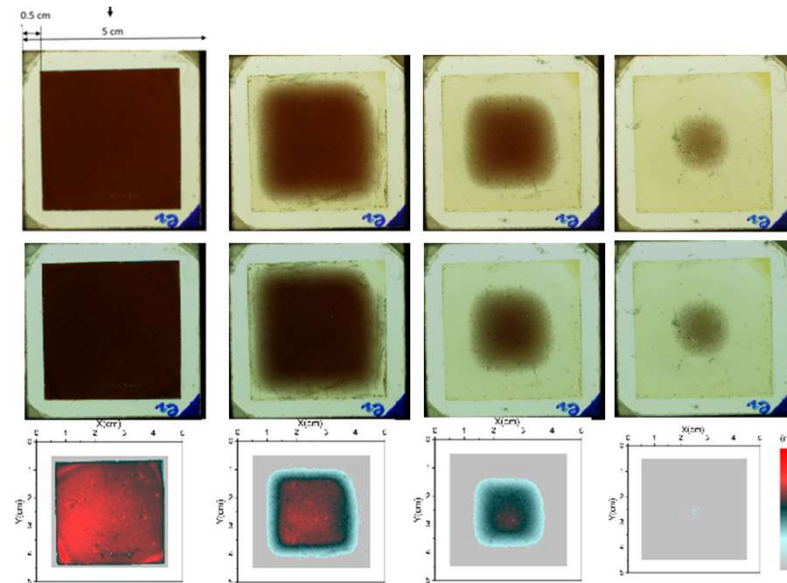
# Side permeation measurement

## Optical test to measure side permeation

E. Booker & al. Energy Technol. 2020, 8, 2000041



Aging at 85°C/85%RH →



Initial correction

Algorithm

N. Naherimaksousi & al. npj Computational Materials volume 7, 190 (2021)

2 phenomena are observed and monitored:

- Surface loss related to the water side ingress (clear border)
- Thickness loss of photo-active PVK in the center

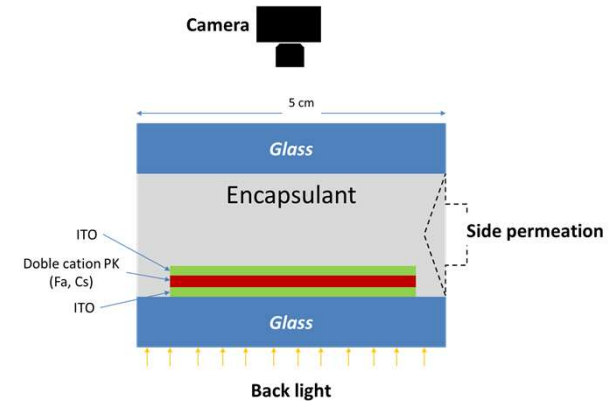
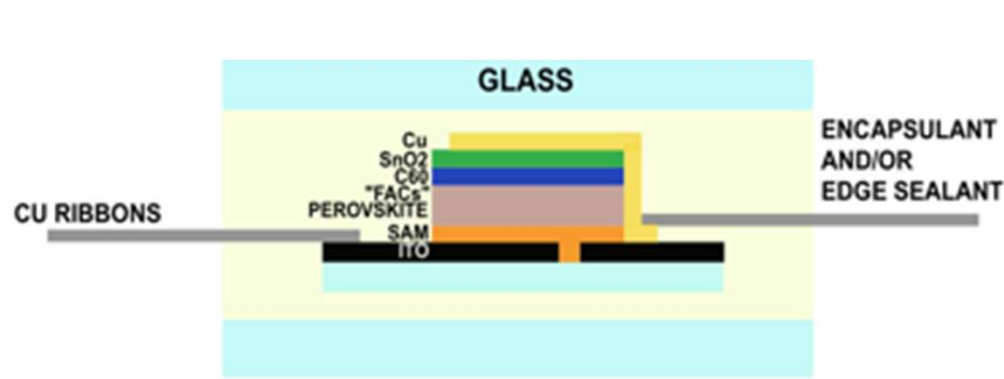


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# HZB/CEA joint experiments (published soon)

Quiterie Emery, Lea Dagault, Mark Khenkin, Stephane Cros, Nikoleta Kyranaki, Max Bernardes, Ulas Erdil, Matthias Demuylder, Rutger Schlatmann, Bernd Stannowski, Carolin Ulbrich



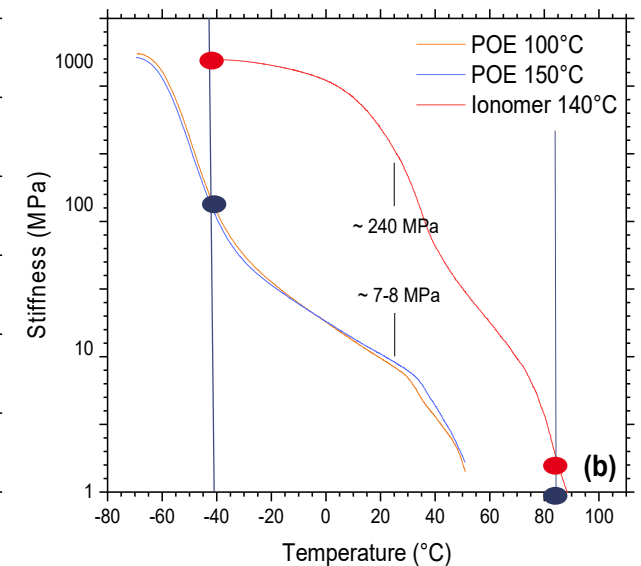
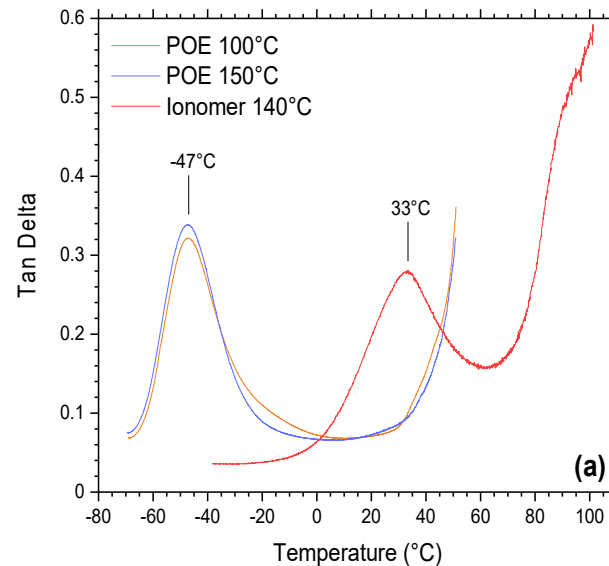
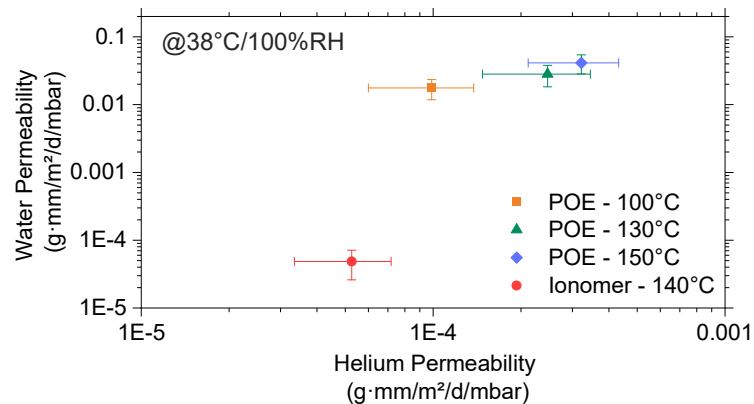
## 2 types of encapsulant: POE or Ionomer, 1 Butyl edge sealant :

- Gas barrier measurements, thermo-mechanical characterization (DSC and DMA)

## PVK solar cells (HZB) and Samples for Side permeation study (Optical test):

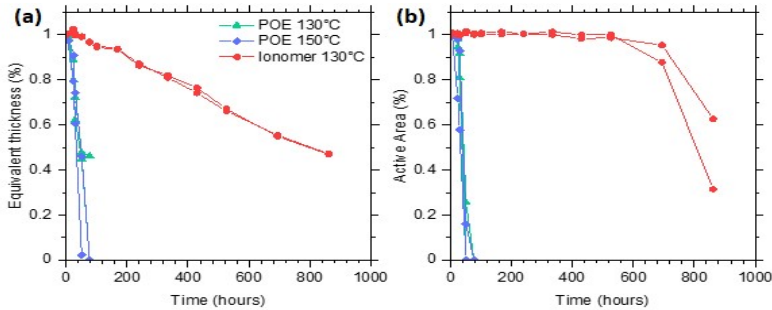
- Encapsulation by hot vacuum lamination or hot press
- Damp heat (85°C/85%RH) and thermal cycling (-40°C/85°C)

## Gas barrier measurements, thermo-mechanical characterization (DSC and DMA)



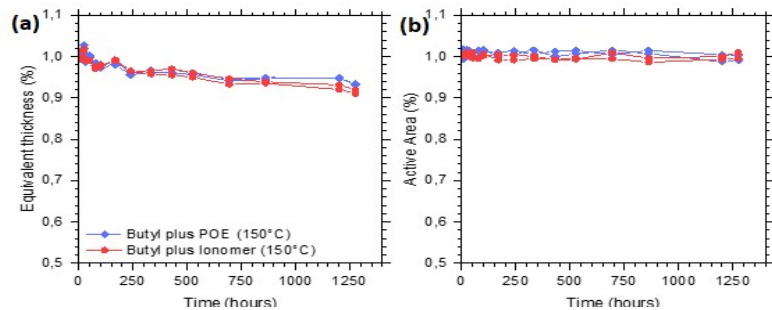
- Gas barrier properties of Ionomer encapsulant are considerably better than those of POE.
- After crosslinking, the gas barrier properties of POE looks a bit degraded!
- Ionomer: glass transition at 33°C and drastic change in the rigidity over 1 thermal cycle (-40/+85°C)
  - Ionomer stiffness covers a breadth of 1000 MPa against 100 Mpa for POE
  - The ionomer causes more shear stress within the PVK stack and could lead to delamination

# Side permeation @ 85°C/85%RH



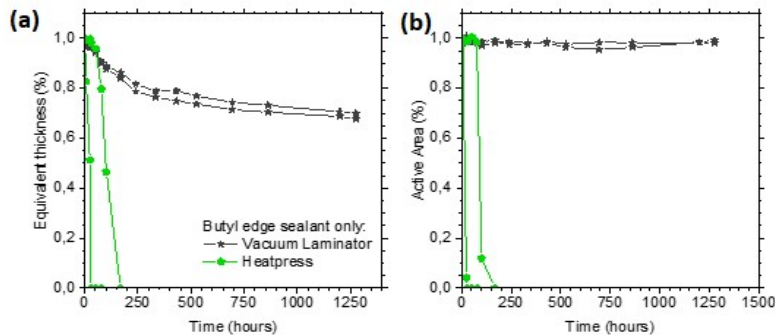
Only encapsulant

- Rapid drop of the PVK area and thickness with POE
- Regular decrease of the equivalent photoactive PVK thickness with ionomer.
- The area decrease, from the edge, starts around 500h (considering threshold)



Encapsulant + Edge sealant

- The behaviour is similar whatever the encapsulant.
- No surface loss (considering threshold).
- Around 10% loss of the equivalent photoactive PVK thickness after 1200h

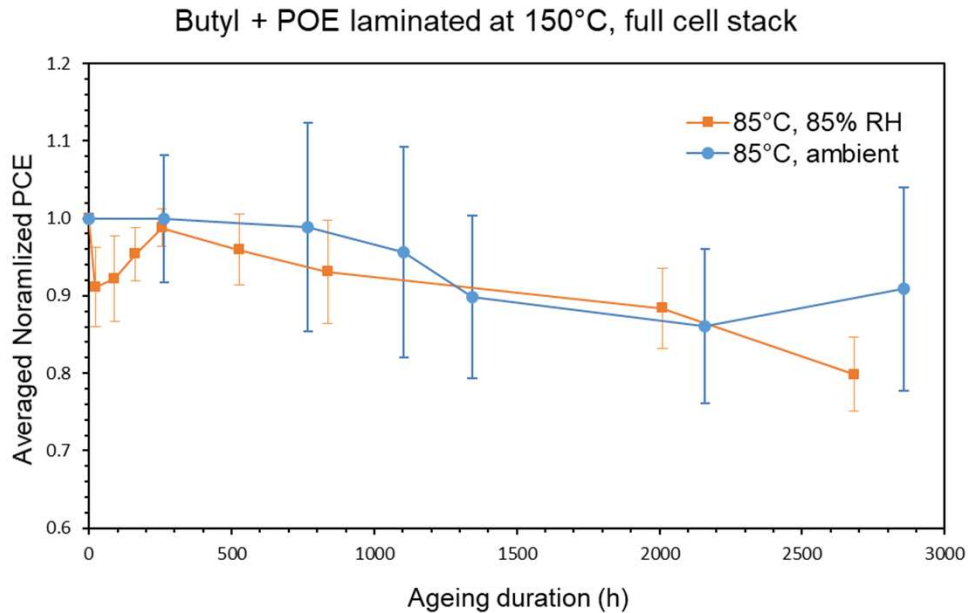


Only edge sealant

- No surface loss (considering threshold) with the vacuum lamination process
- Lack of adhesion with the heat press.
- The use of only edge sealant leads to a more rapid thickness loss as compared to the combination edge sealant/encapsulant



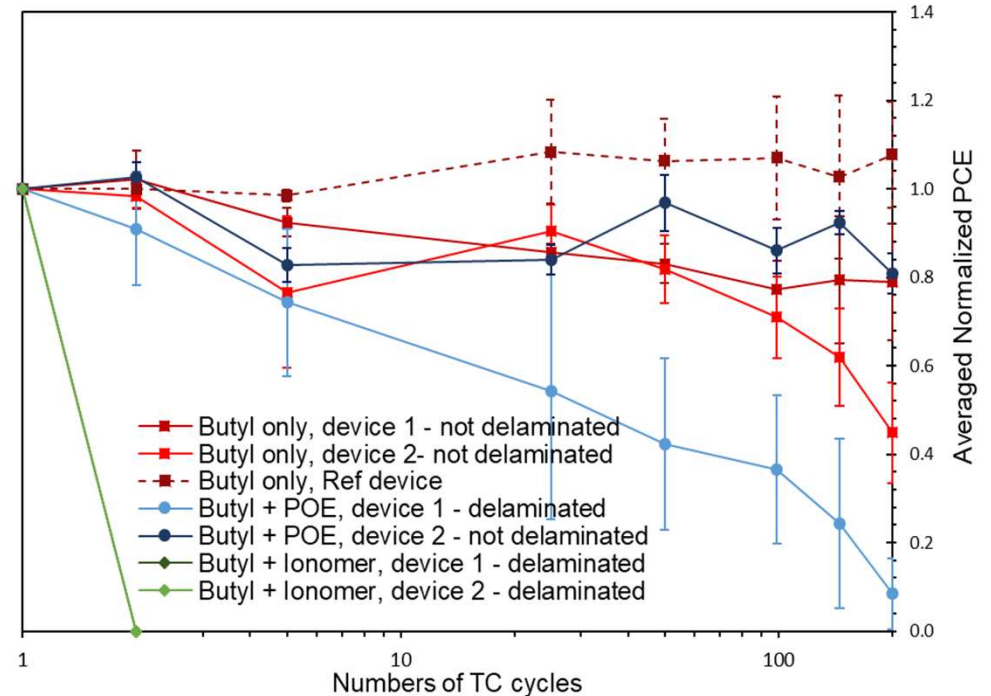
## Damp heat aging (85°C, 85%RH)



- The degradation is related to temperature, no water ingress.
- The losses (around 10%) are similar to those observed with the optical test

## Thermal cycling (-40°C/+85°C)

Full cell stack



- Full and rapid delamination with ionomer.
- With POE, some delamination are observed with 1 sample. The degradation is comparable to “only edge sealant” for the over one.

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# Gas barrier adhesives

ARKEMA



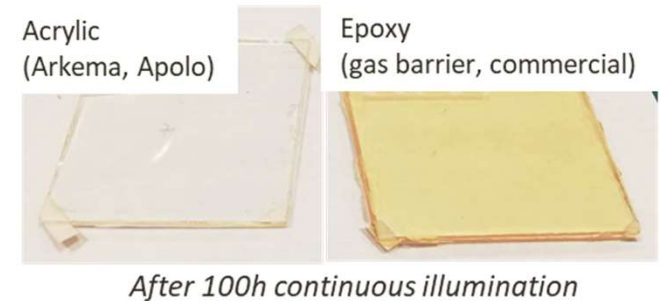
## Development of gas barrier flexible glue with Arkema

Development of a **photocurable flexible liquid encapsulant**

- Low water vapor transmission rate (below  $2\text{g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ )
- Fast polymerisation process under UV
- Flexible with low radius of curvature
- No yellowing

Acrylic based, using Arkema proprietary nanostructured block copolymers for optimal adhesion and flexibility

We demonstrated gas barrier performances close to rigid epoxy gas barrier grades without yellowing and better flexibility

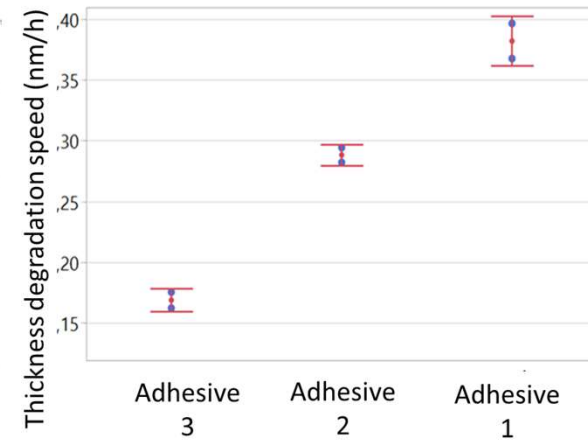
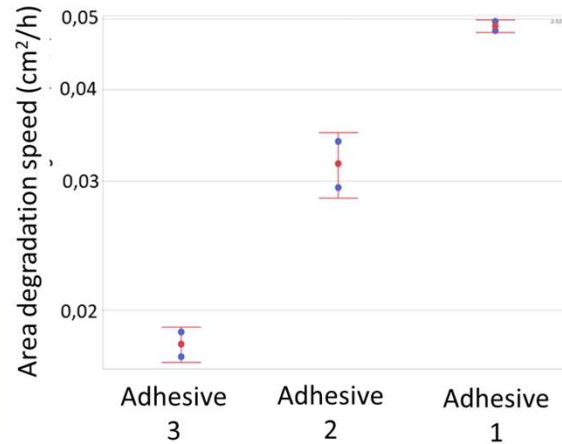
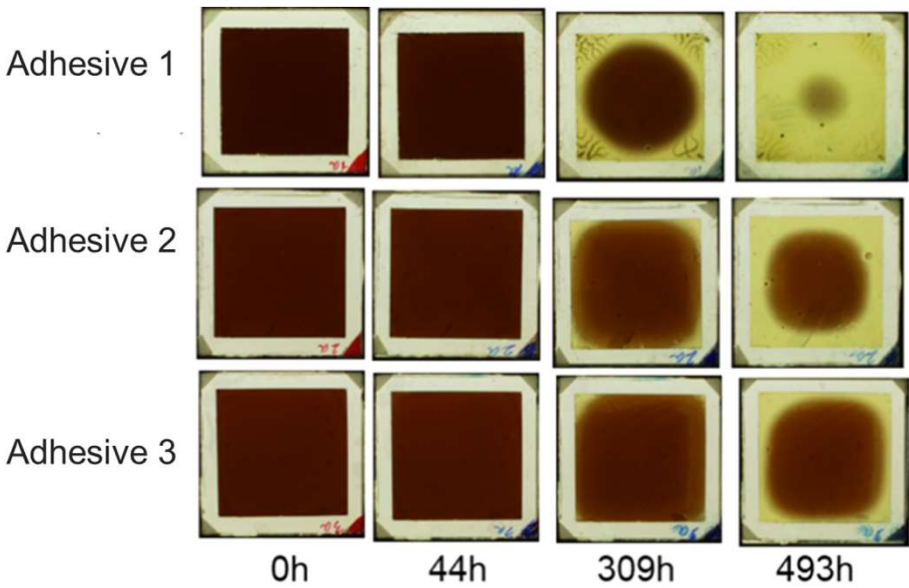






# Gas barrier adhesives

Use of a given architecture and composition to check the effectiveness of the encapsulant (UV glue with Arkema)



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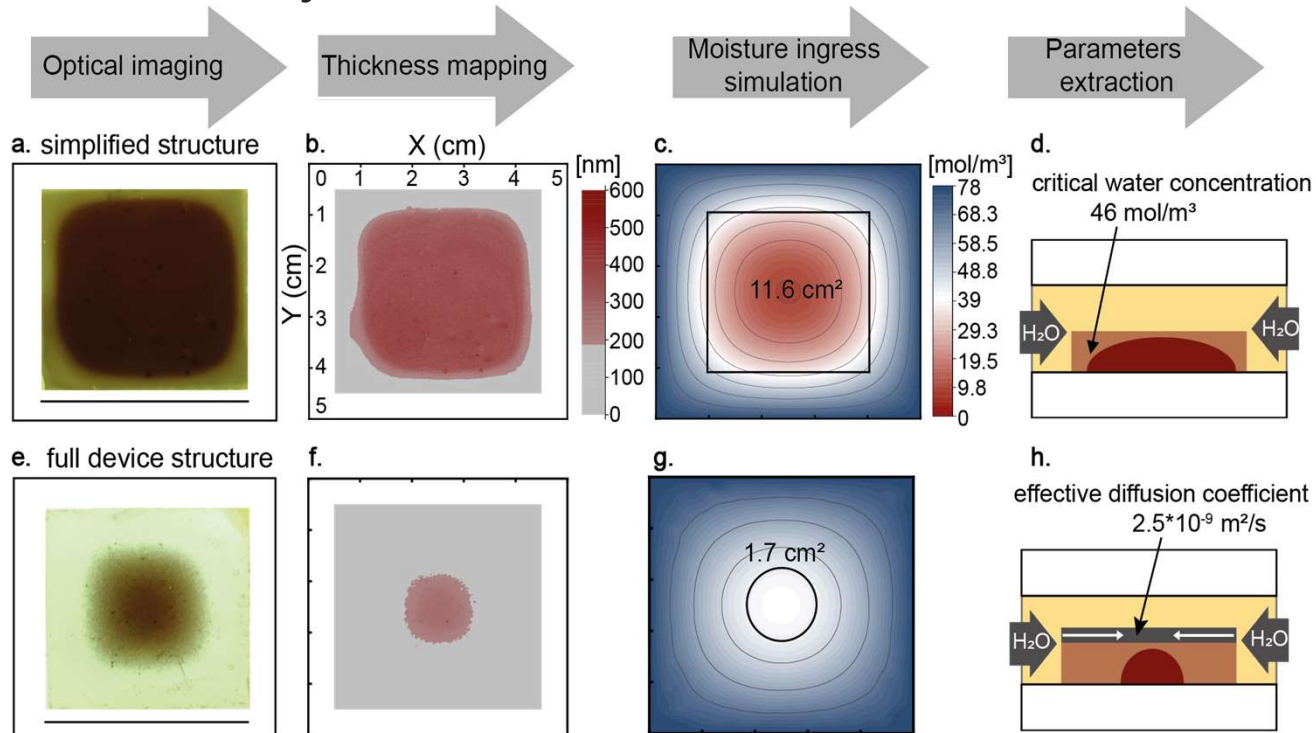


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# Side permeation measurement

Check of the insertion of interlayers impact with a given encapsulant:  
SnO<sub>2</sub> and PTAA interlayers in a NIP architecture



Mathis Majorel,  
Nikoleta Kyranaki,  
Mathilde Fievez,  
Nina Taherimakhsoosi,  
Stéphane Cros  
(CEA/Arkema/University of British Columbia)



# Thanks to



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<https://www.viperlab.eu/>

Contact me: [stephane.cros@cea.fr](mailto:stephane.cros@cea.fr)



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N°101006715