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Self-healing high-temperature functional glass for hydrogen fuel cell sealing

François O. MÉAR

PhD: Raphaël VOIVENEL (ANR CELCER EHT), Daniel COILLOT (ULille), Sandra CASTANIÉ (DGA)
Renaud PODOR (CEA-ICSM), Lionel MONTAGNE (ULille)

Outline

- ✓ **Glass-sealant for SOFC/SOEC technology: state of the art**

  (SOFC: Solid Oxide Fuel Cell / SOEC: Solid Oxide Electrolysis Cell)

- ✓ **Self-healing: background – definition**
- ✓ **Non-autonomous & autonomous self-healing concepts**
- ✓ ***Applications*: self-healing in glassy sealant**
  - ✓ **Non-autonomous self-healing processing in viscous seal**
  - ✓ **Autonomous self-healing concept for rigid seal**
- ✓ **Conclusions**

Comparison of fuel cell technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Challenges
Polymer Electrolyte Membrane (PEM)*	Perfluoro sulfonic acid	50-100°C 122-212°F typically 80°C	1 kW–100 kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transportation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10–100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW–3 MW 300 kW module	45-50%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature corrosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	700-1000°C 1202-1832°F	1 kW–2 MW	60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell components • High temperature operation requires long start up time and limits

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 250 W and operating at 60-90°C.

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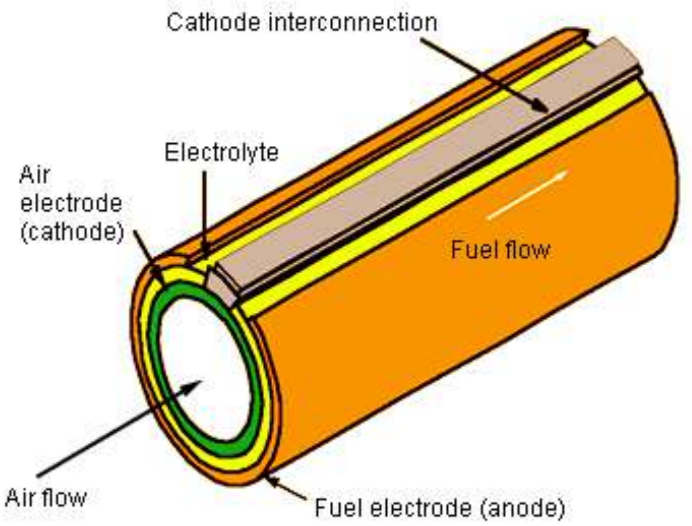
*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 250 W and operating at 60-90°C.

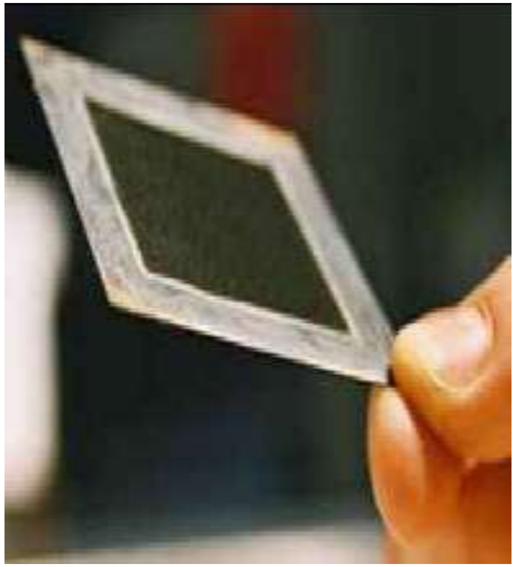
- SOFCs are made up of very thin layer of ceramics.
- Ceramics used in SOFCs do not become electrically and ionically active until they reach 500-1000°C and the high temperature enables them to oxidize nearly any fuel.
- Solid electrolyte is made from a ceramic material called Yttria-Stabilized Zirconia (YSZ).
- Best suited for large applications although research continues to develop lower temperature SOFCs for use in vehicles.

SOFC/SOEC design



Tubular Siemens-Westinghouse

Planar Global



Metal supported thin film
Ceres Power

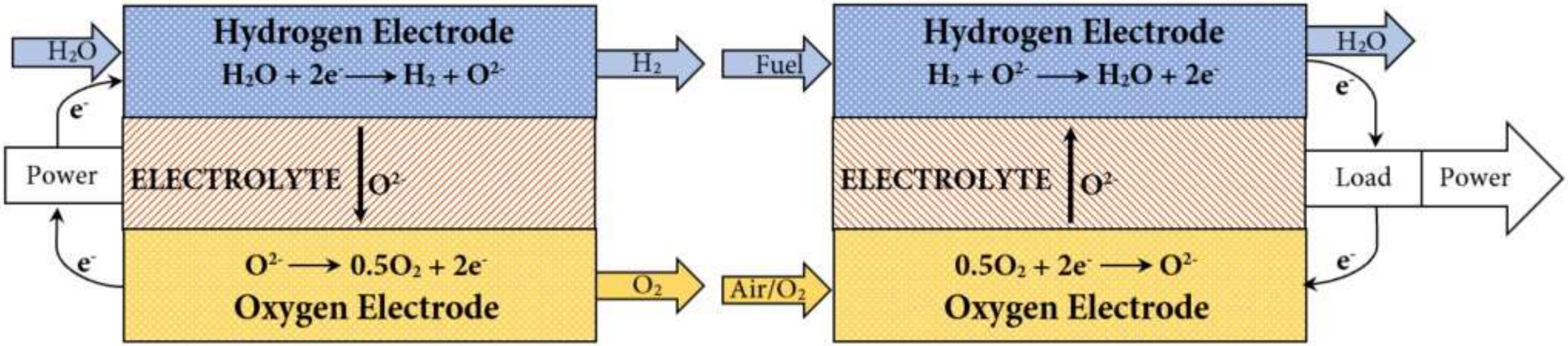
HT-SOFC
1000°C

Advantages sealing durability

IT-SOFC
550°C

SOEC vs SOFC difference

Solid Oxide Electrolysis Cell (SOEC) | **Solid Oxide Fuel Cell (SOFC)**



Cathode reaction: $H_2O + 2\ e^- \rightarrow H_2 + O^{2-}$

Anode reaction: $O^{2-} \rightarrow ½\ O_2 + 2\ e^-$

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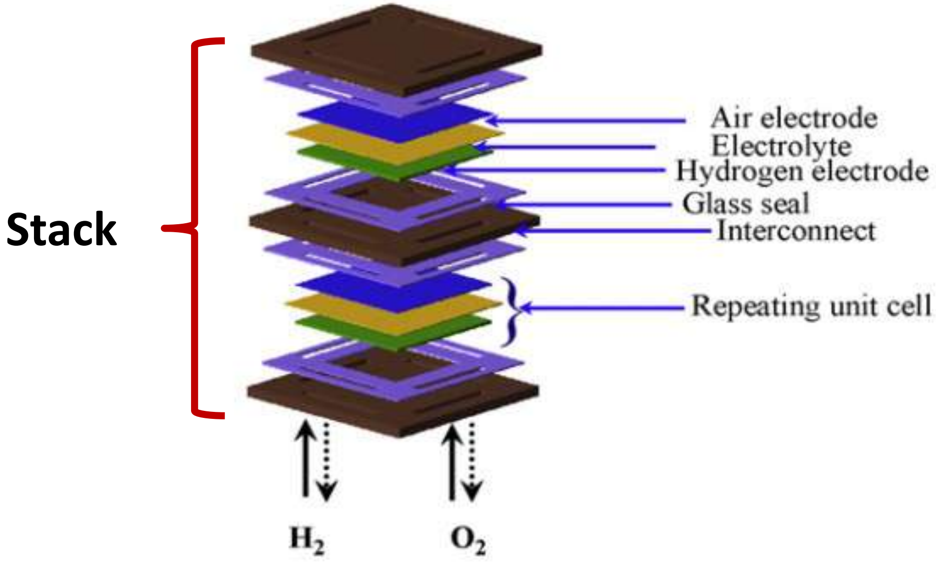
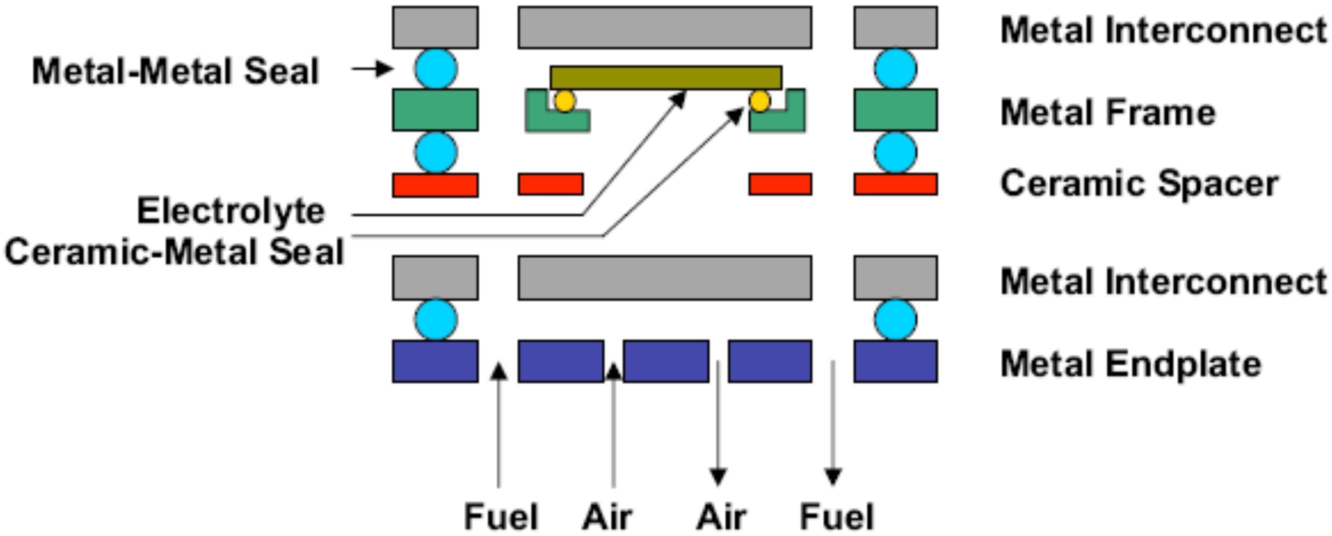
Glass sealant for SOFC/SOEC technology



Fuel cell design by Jüllich (Germany)



Requirements of a SOFC/SOEC seal

Properties	Requirements
Thermal properties	- **Thermal expansion coefficient at 9.5 – 12.0 × 10^{-6} °C^{-1}** - Thermally stable ~ 5,000h for mobile applications and for ~ 50,000h for stationary applications at 650-900°C cell operating temperatures
Chemical properties	- Resistant to vaporization and compositional change in stringent oxidizing and wet reducing atmospheres at 650-900°C - **Limited or no reaction with other cell components**
Mechanical properties	- Withstand external static and dynamic forces during transportation and operation - **Resistant to thermal cycling failure during start-up and shut-down of cell stacks**
Electrical properties	- **Electrical resistivity ≥ 10^4 Ω.cm at operating temperature** - Electrical resistivity greater than 500 Ω.cm between cells and stacks at nominal stack operating condition (0.7 V at 500-700 mA/cm^2)
Sealing ability	- Sealing load < 35 kPa - Withstand differential pressure up to 14-35 kPa across a cell or stack - **Total fuel leakage < 1% for the duration of the cell life**
Fabrication flexibility	- Flexible design, low processing cost, and high reliability

Advantages & disadvantages of different types of seals

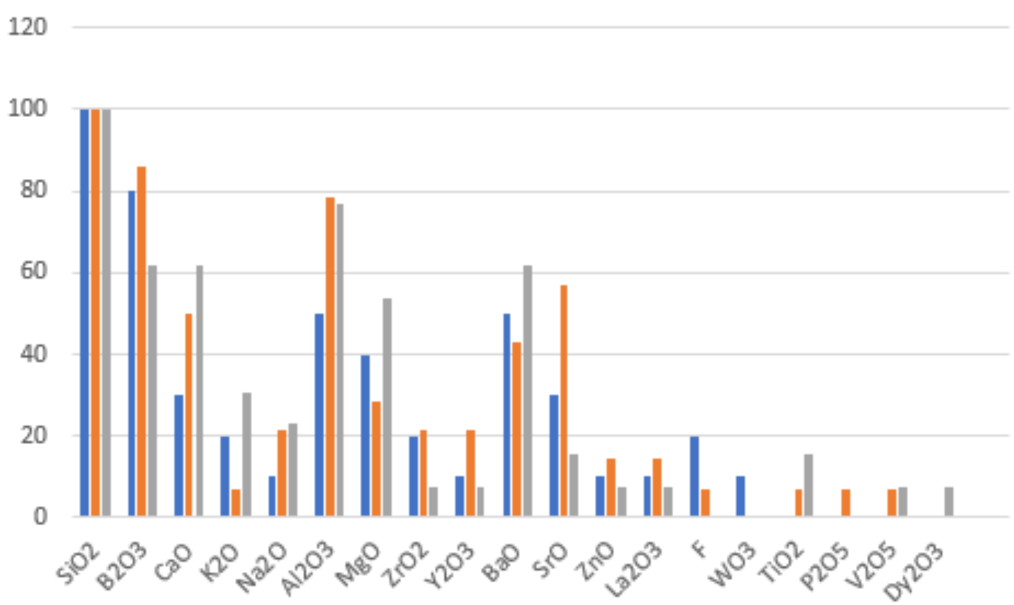
Seal type	Advantages	Disadvantages
Compressive seal	Easy replacement of seals in a manufacturing cell stack Resistance to thermal cycling	Application of external load Complex design and high cost High gas leakage rate Unsuitable for mobile applications Poor stability Electrically conductive
Viscous seal	**Low thermal cycle**	**Non-wetting with other SOFC/SOEC components** **Poor oxidation resistance** Hydrogen embrittlement Electrically conductive
Rigid seal	**Hermetic sealing** Tailoring performance by composition design **High electrical resistivity** Suitable for stationary and mobile applications Flexible in design and fabrication	**Brittle at low temperatures → poor resistance to thermal cycling** **Chemical reaction with other cell components**

Functions of different oxide in a seal glass

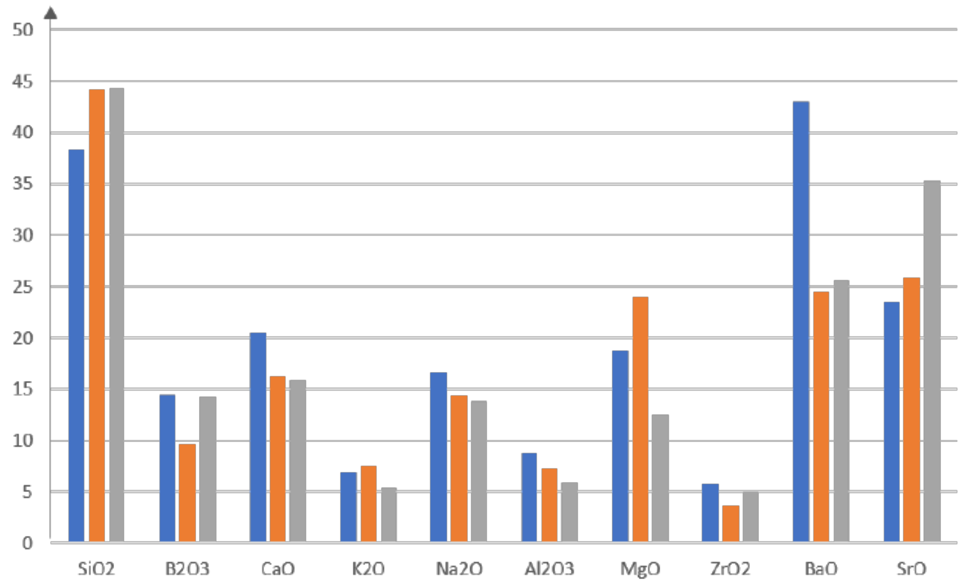
Glass constituent	Oxide	Function
Network former	**SiO_2**, **B_2O_3**	Form glass network Determine T_g and T_s Determine thermal expansion coefficient Determine adhesion/wetting with other SOFC/SOEC components
Network modifier	Li_2O, **Na_2O**, K_2O **BaO**, **SrO**, **CaO**, MgO	Maintain charge neutrality Create non-bridging oxygen species Modify glass properties such as T_g, T_s and thermal expansion coefficient
Intermediate	**Al_2O_3**, Ga_2O_3	Hinder devitrification Modify glass viscosity
Additive	La_2O_3, Nd_2O_3, Y_2O_3 ZnO, PbO NiO, CuO, CoO, MnO Cr_2O_3, V_2O_5 TiO_2, ZrO_2, P_2O_5	Modify glass viscosity Increase thermal expansion coefficient Improve glass flowability Improve seal glass adhesion to other cell components Induce devitrification

Evolution from 2020 to 2022

Constituents evolution in glass seal



Composition evolution in glass seal



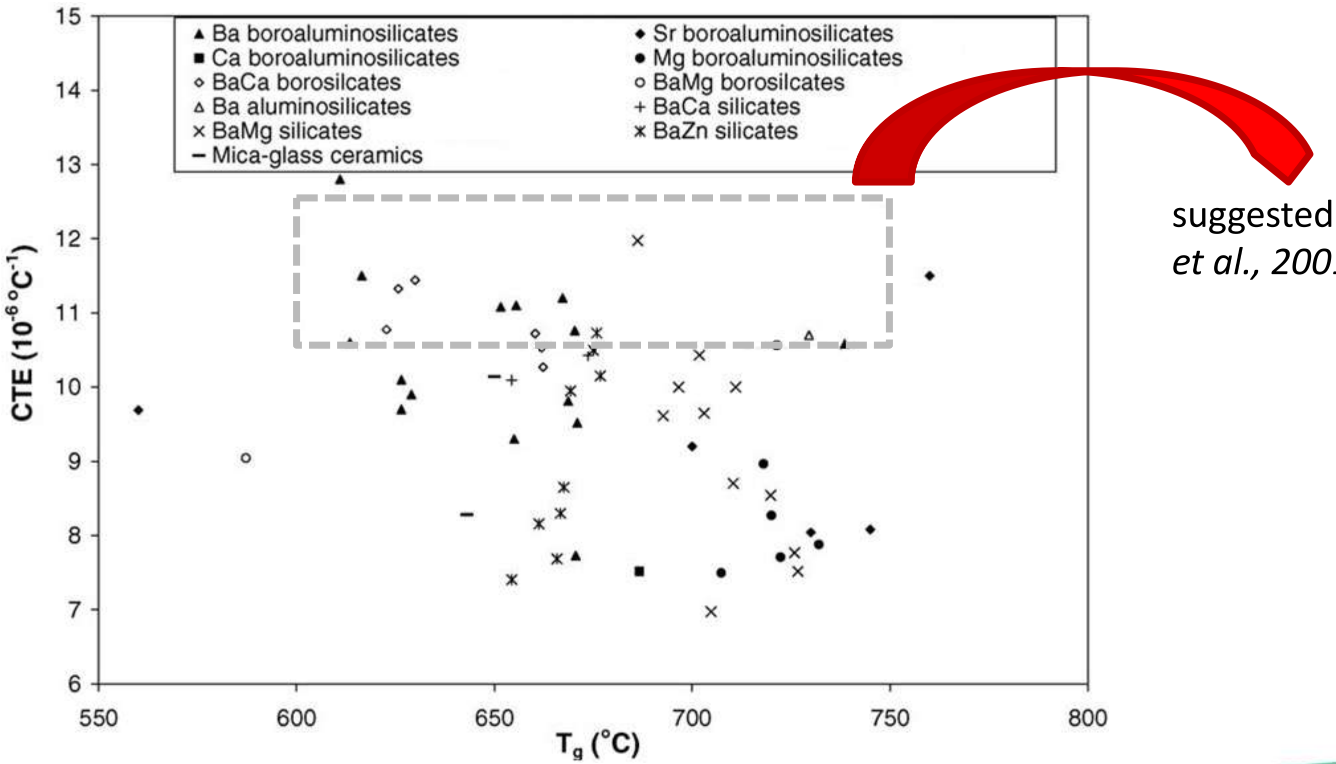
2020 **2021** **2022**

Glass sealants for SOFC/SOEC

<u>**Two important criteria for selection of a suitable glass sealant**</u> :

⇒ **glass transition temperature, T_g** (because of the glass must flow sufficiently to provide an adequate seal, while maintaining sufficient rigidity for mechanical integrity)

⇒ **coefficient of thermal expansion, CTE** (must match other cell components electrolyte and the interconnect material, to minimize thermal stresses)



suggested by *Geasee et al., 2001*

From J. W. Fergus, J. Power Source, 2005

Application: *self-healing in glassy sealant*

Degradation of components

- Degradation of single cell
- Degradation of sealing
- Oxidation of interconnects
- Degradation of contact resistances
- Interaction between
  - Glass / interconnect
  - Interconnect / cell
  - Contact layer / interconnect
  - Contact layer / cell

Design/System specific degradation

- Formation of hot-spots
- Inhomogeneous fuel gas distribution / utilization
- Soot formation
- Degradation due to unfavorable stack integration into system
- Degradation due to unfavorable stack-preload (especially for IC-cassettes from pressed ferritic steel)

Key points:
- **long term chemical stability**
- **stability against crystallization, control of phase formation**
- **mechanical stability (prevent crack formation)**

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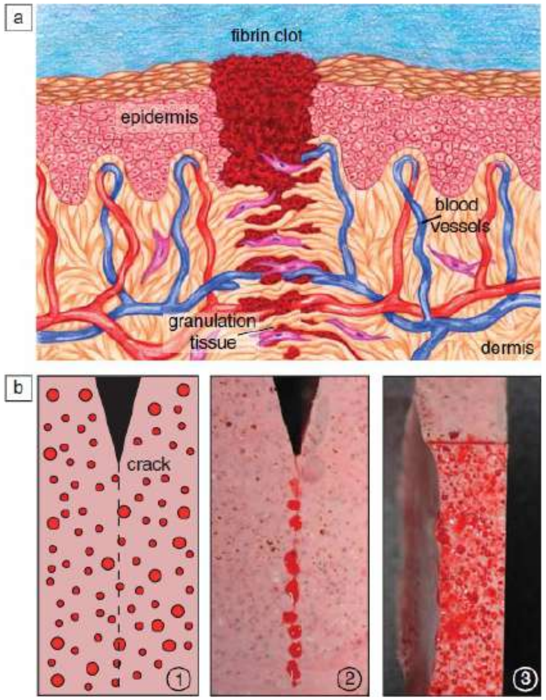
Self-healing is proposed as a solution to decrease gas leaks due to cracks

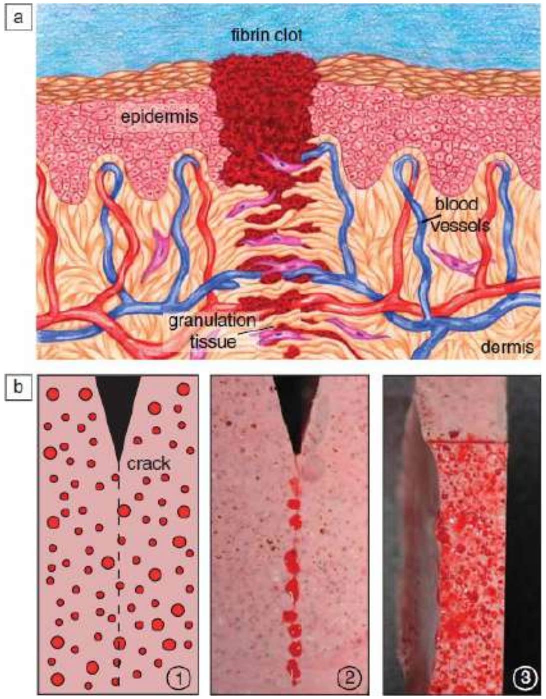
Self-healing: *background*



(a) Schematic of an intermediate stage of biological wound healing in skin
(b) Demonstration of bio-inspired damage-triggered release of a microencapsulated healing agent in a polymer

From J.P. Youngblood, MRS Bull. 2008

Self-healing: *background*



(a) Schematic of an intermediate stage of biological wound healing in skin
(b) Demonstration of bio-inspired damage-triggered release of a microencapsulated healing agent in a polymer

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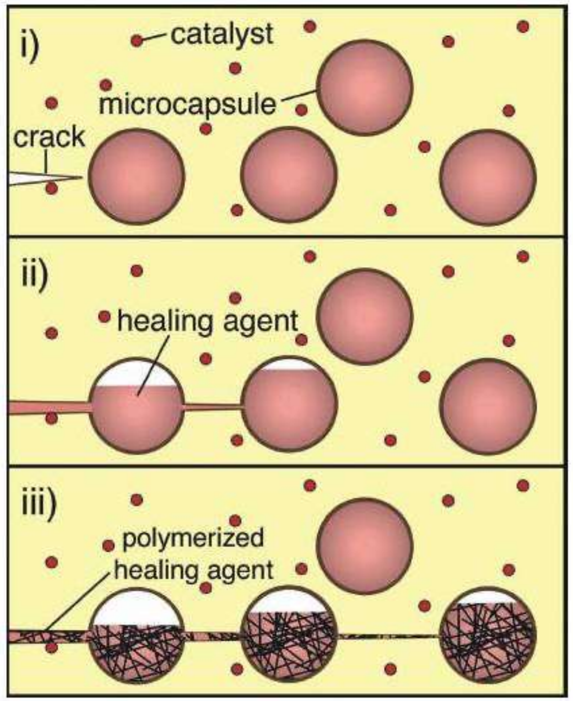
(i) Cracks form in the matrix wherever damage occurs.

(ii) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action.

(iii) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.



From S.R. White et al., Nature 2001

Self-healing: *definition*

<u>Self-healing material</u>: material able to heal (repair) automatically and autonomously damages occurring during processing.

Thus, self-healing can be of the following two types :

→ **autonomous**: without any intervention
→ **non-autonomous**: needs human intervention / external triggering

Numerous field of applications:

- polymers
- composites materials for aerospace applications
- microelectronic packaging
- medical uses
- concrete or cementitious structures

Non-autonomous self-healing: *glassy seal*

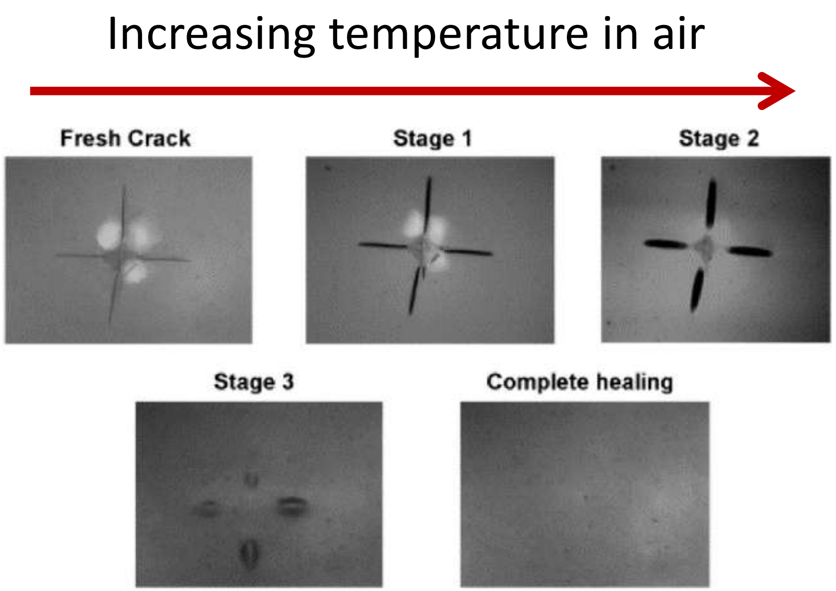
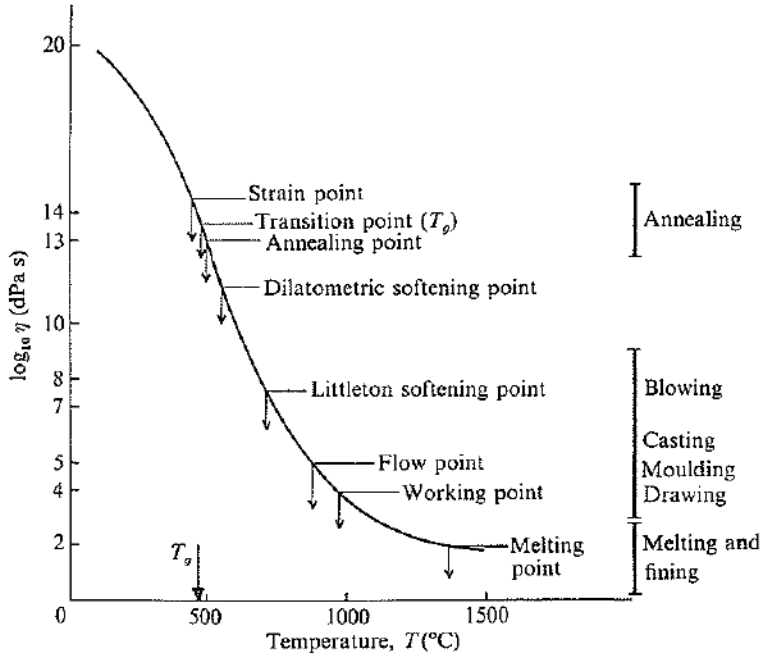


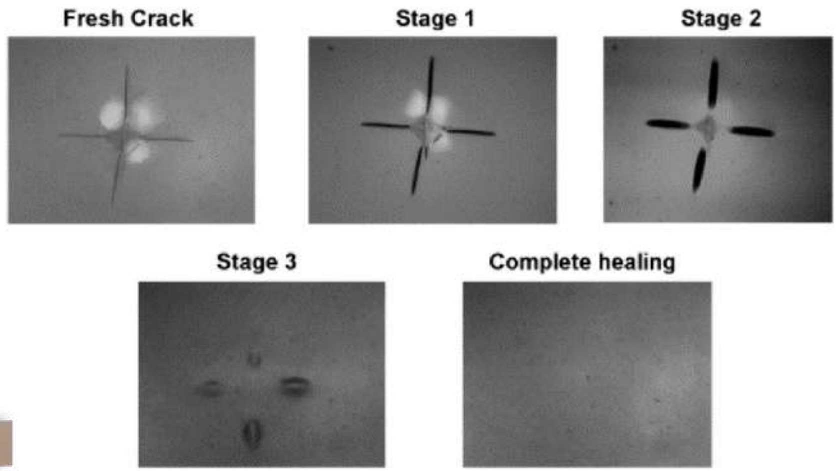
Fig. 4. Self-healing behavior of glass B indicating several stages of self-healing of cracks introduced by the microindentation technique (× 400) magnification.



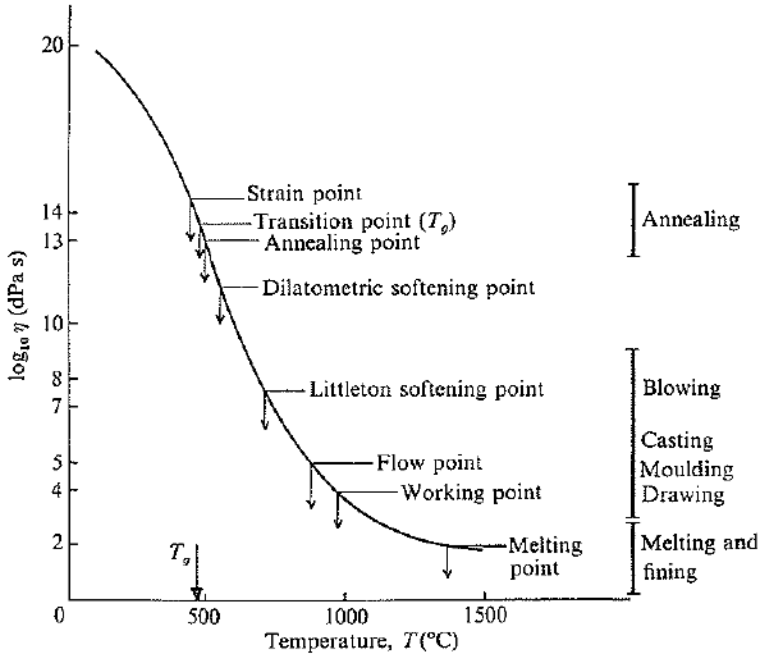
From R.N. Singh, Appl. Ceram. Techno. 2007

Non-autonomous self-healing: *glassy seal*

Increasing temperature in air



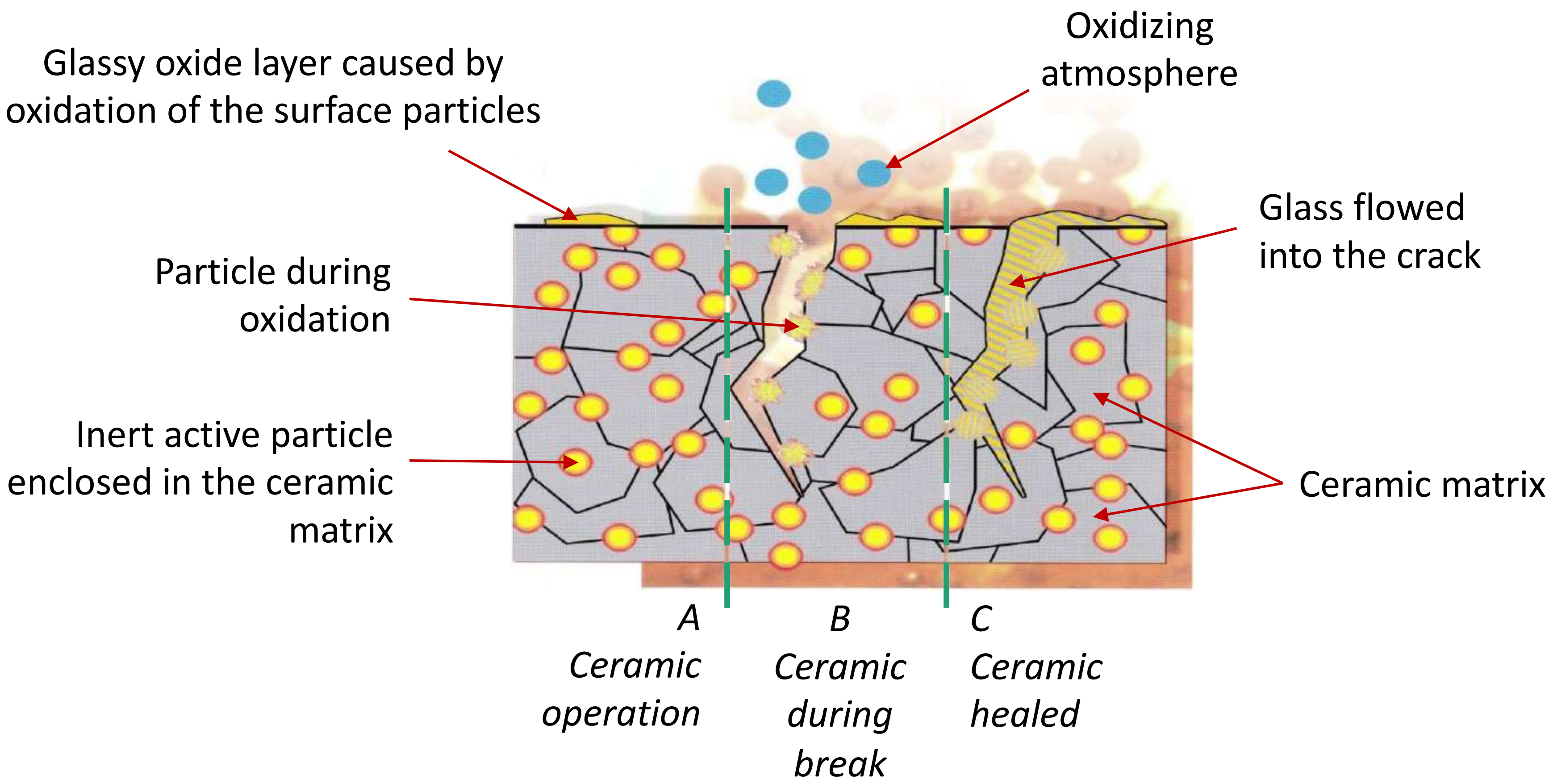
4. *Self-healing behavior of glass B indicating several stages of self-healing of cracks introduced by the microindentation technique × 400) magnification.*



From R.N. Singh, Appl. Ceram. Techno. 2007

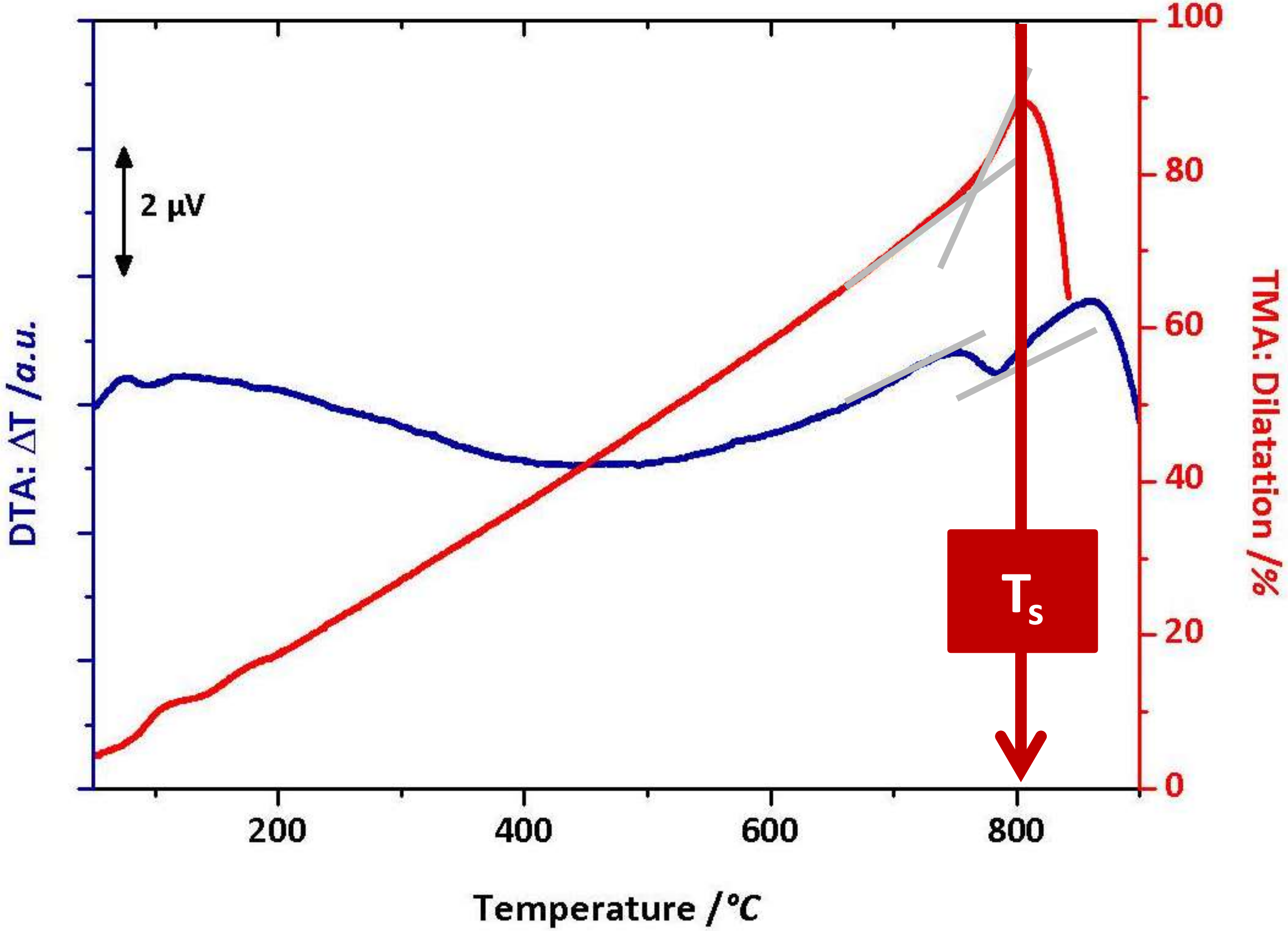
disappearance of damage due to the flow of the glass phase after heating at high operating temperature

Autonomous self-healing: *ceramic composite*

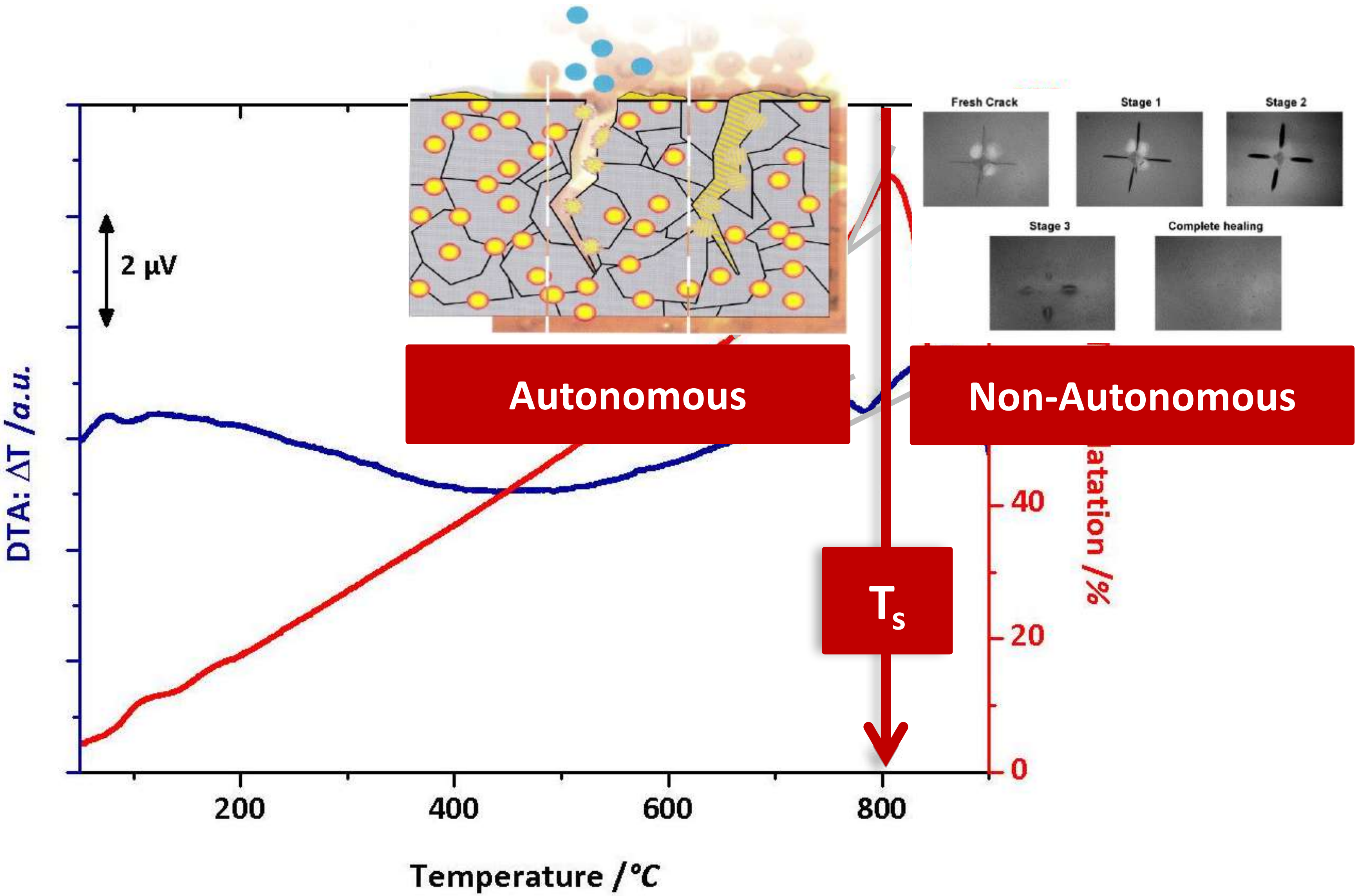


From S.K. Ghosh, Self Healing Materials: Fundamentals, Design Strategies and Applications, Willey-VCH 2009

Self-healing glassy materials: *concept*



Self-healing glassy materials: *concept*



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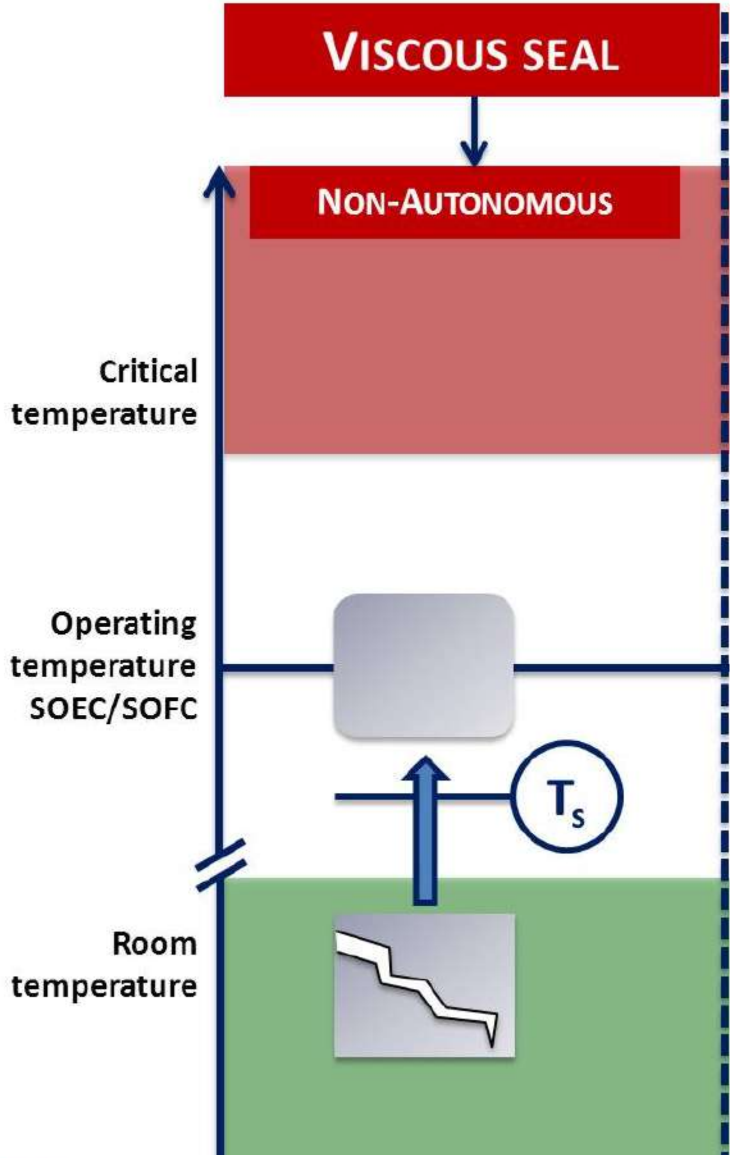
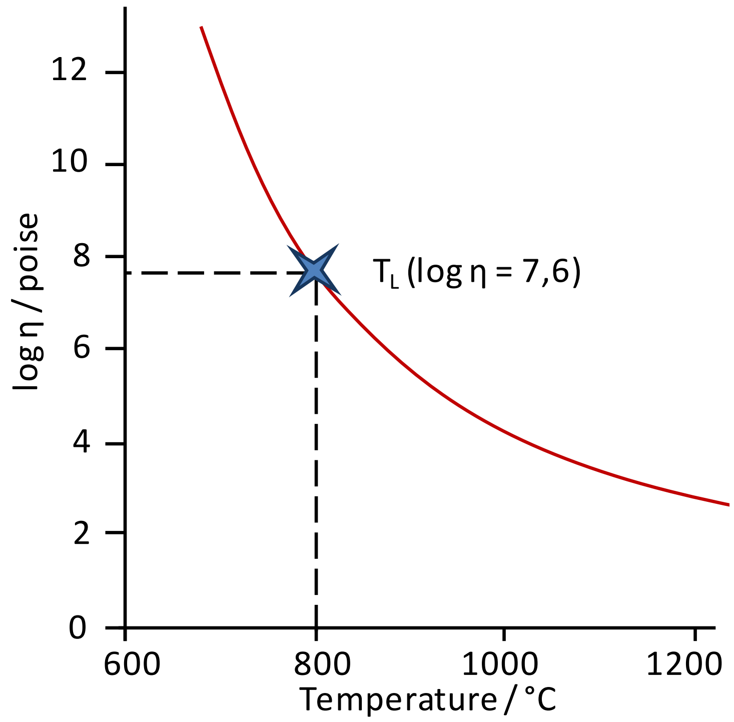


Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ (η = $10^{7.6}$ Poise) = 800˚C
→ Low viscosity at 900˚C
→ No crystallization at 800˚C
→ Limited interactions with other components of electrochemical systems



Selection criteria (Sciglass software)

→ T_g > 600˚C
→ 750˚C < $T_{Littleton}$ < 900˚C
→ TEC > 5 × 10^{-6} K^{-1}
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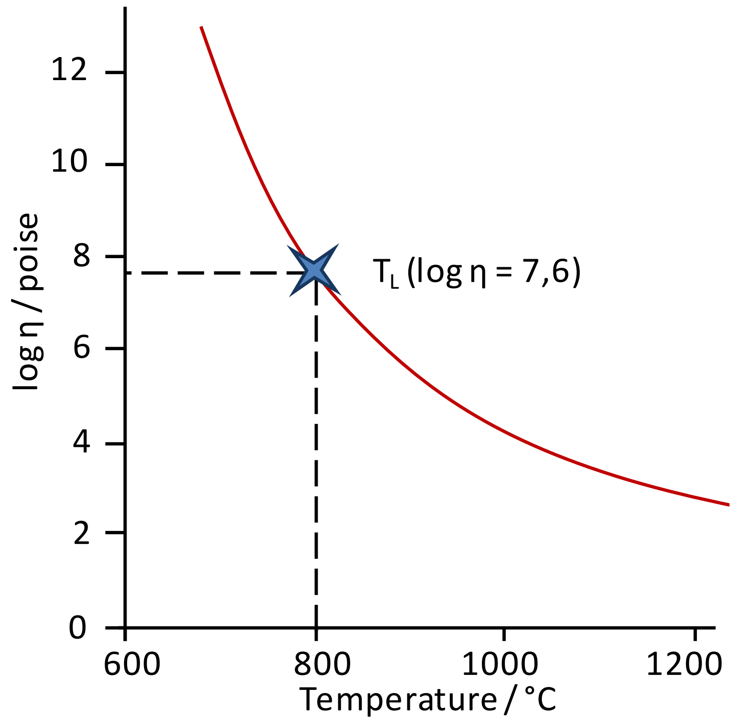

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Molar %	SiO_2	ZrO_2	B_2O_3	Al_2O_3	Ga_2O_3	La_2O_3	Y_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	MgO	SrO	Crystallisation	T_g / °C
Vsc1	70.24	-	1.92	5.26	-	-	-	3.60	1.19	0.60	3.32	9.05	4.82	-	Yes	650
Vsc2	63.30	-	-	-	-	-	4.99	20.72	6.81	4.45	-	-	-	-	Yes	566
Vsc3	67.46	13.34	-	-	-	1.03	-	13.67	4.50	-	-	-	-	-	No	765
Vsc4	61.39	-	6.14	-	14.34	-	-	13.67	4.46	-	-	-	-	-	No	580
Vsc5	66.01	3.43	5.57	4.21	-	-	-	2.16	0.71	12.21	-	-	-	5.70	Yes	686

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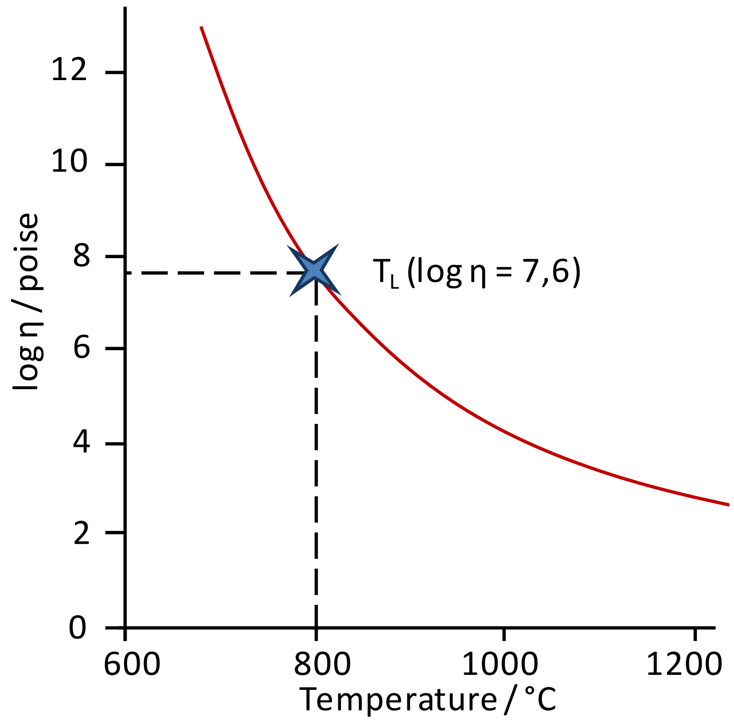

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Vsc3	67.46	13.34	-	-	-	1.03	-	13.67	4.50	-	-	-	-	-	No	765
Vsc4	61.39	-	6.14	-	14.34	-	-	13.67	4.46	-	-	-	-	-	No	580
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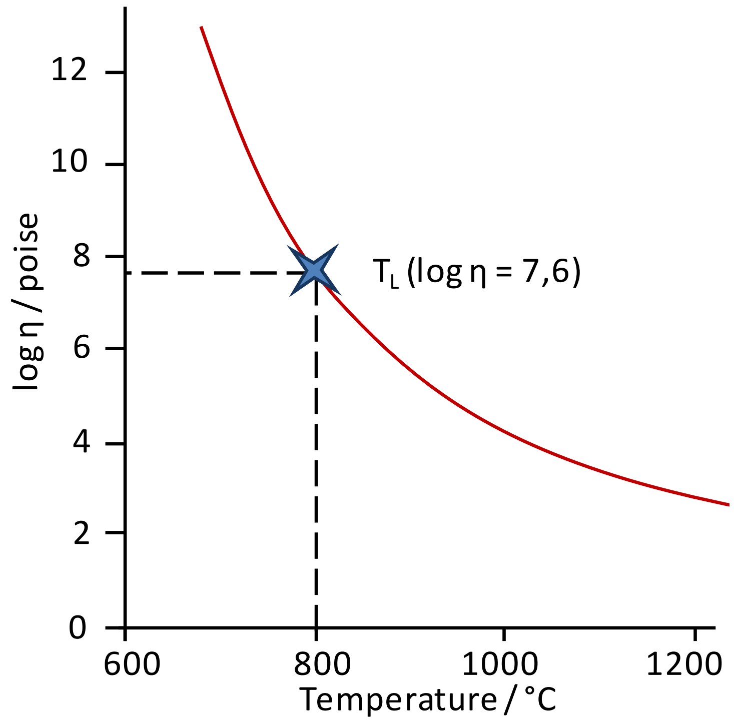

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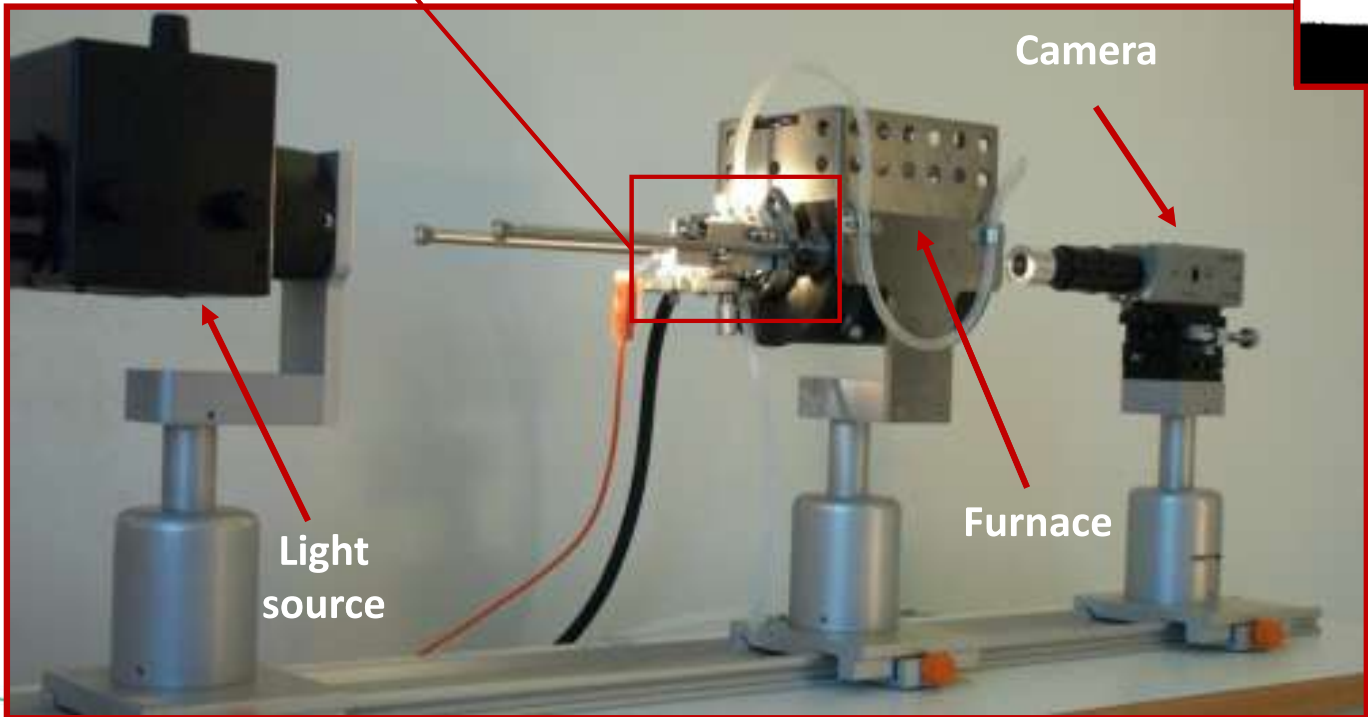
Objective ➡ **decrease of thermal characteristics**

→ ZrO_2 substituted by SiO_2 and/or B_2O_3

Molar %	SiO_2	ZrO_2	B_2O_3	La_2O_3	Na_2O	K_2O	Crystallisation	T_g / °C	T_s / °C
Vsc3	67.46	13.34	-	1.03	13.67	4.50	No	765	854
Vsc31	64.52	7.09	10.03	0.99	13.07	4.30	No	616	675
Vsc32	69.78	7.03	4.98	0.98	12.97	4.27	No	630	692
Vsc33	74.95	6.97	-	0.97	12.87	4.23	No	610	675
Vsc34	65.96	10.14	5.13	1.01	13.36	4.40	No	668	750

Hot-stage microscopy (HSM): *apparatus*

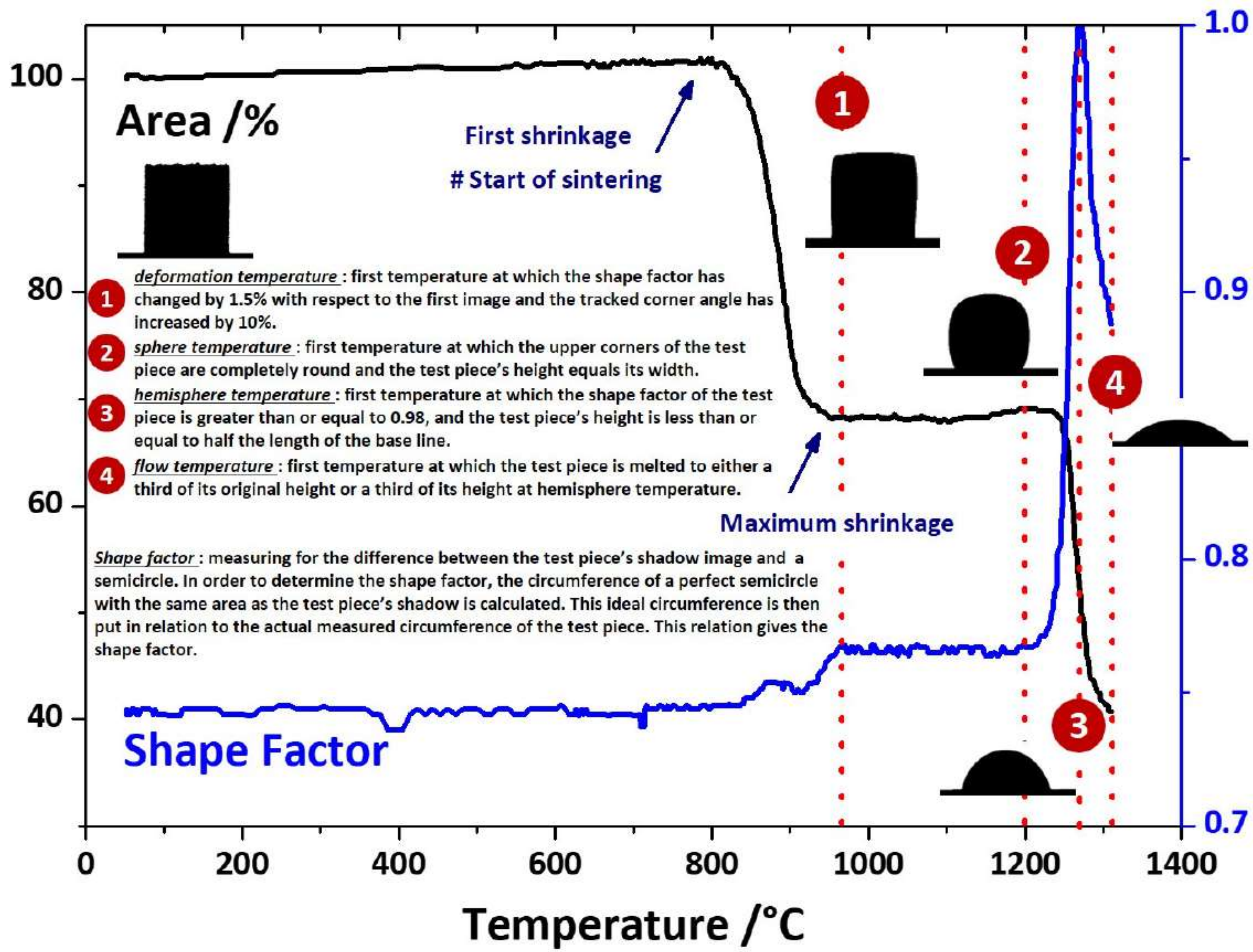
Support sample / thermocouple



Characterization of sample evolution:

→ area (S/S_0)
→ shape factor
→ wettability

Hot-stage microscopy curves



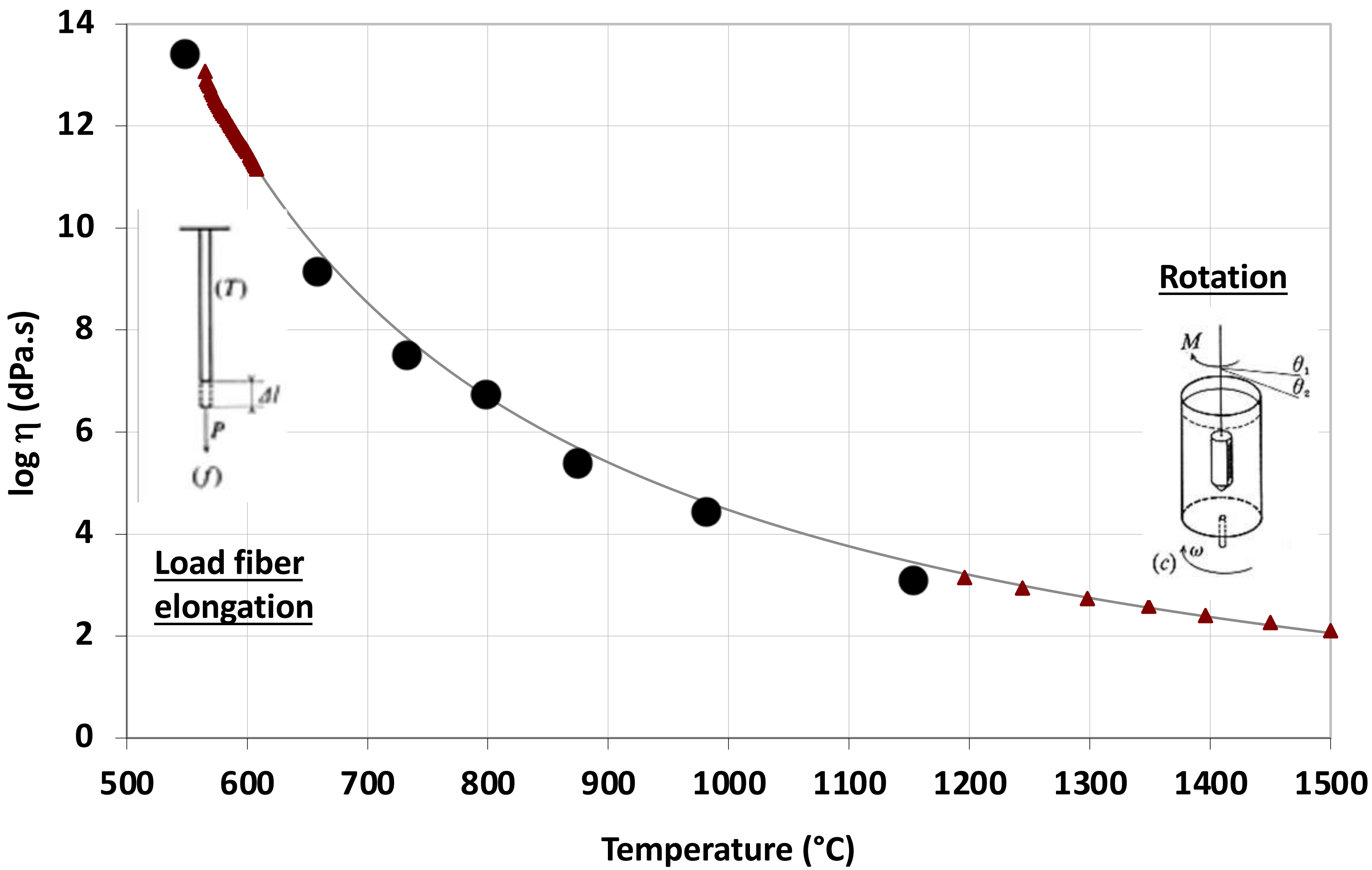
Fixed viscosity points vs. models

Viscosity points	*Scholze* [5] $\log\eta \pm \sigma$ (P)	*Pascual* et al [4] $\log\eta \pm \sigma$ (P)	*This work* $\log\eta \pm \sigma$ (P)
First shrinkage	10·0±0·3	8·9±0·25	9·1±0·1
Maximum shrinkage	8·2±0·5	7·9±0·2	7·8±0·1
Deformation	6·1±0·2	6·6±0·1	6·3±0·1
Sphere	-	-	5·4±0·1
Half ball	4·6±0·1	4·5±0·1	4·1±0·1
Flow	4·1±0·1	3·1±0·15	3·4±0·1

qualitative **quantitative**

From Pascual et al., Phys. Chem. Glasses 2005

Example: *Schott 8422*



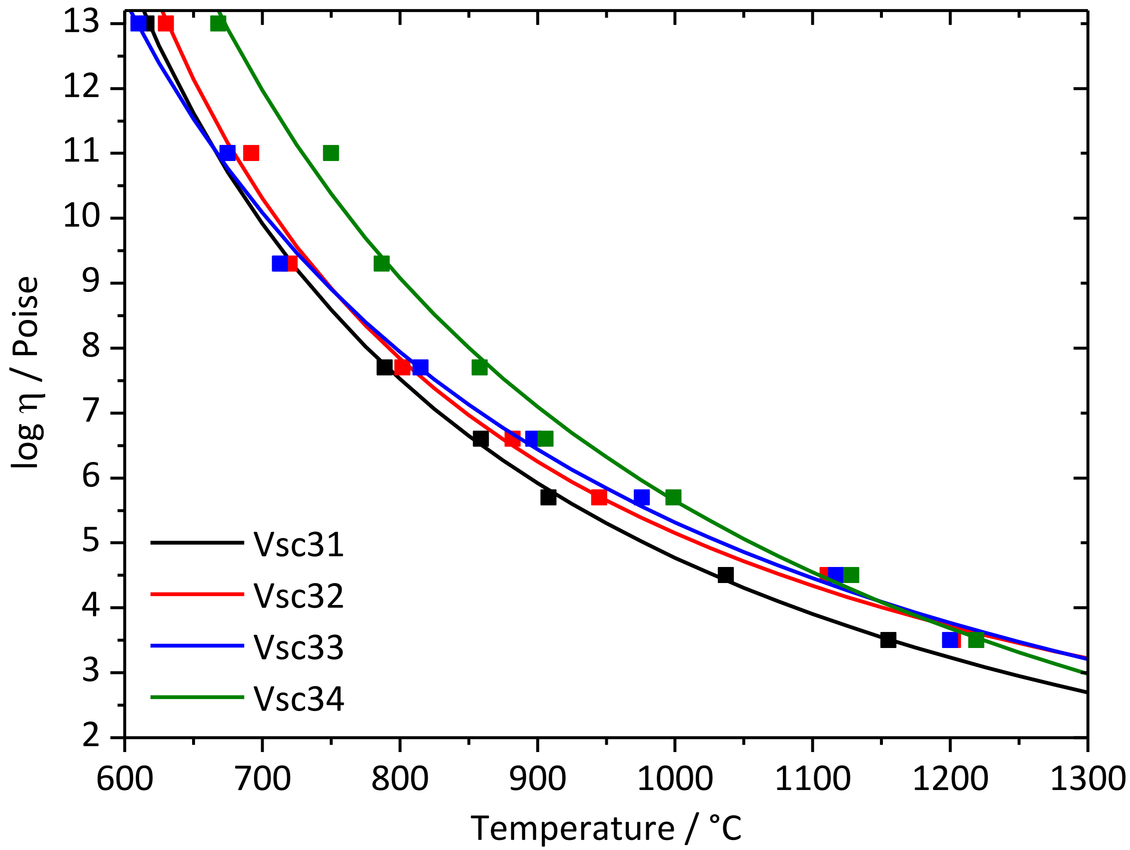
Viscous seal for SOEC

HSM measurements: *viscosity*

→ Applying the method to Vsc glasses

→ Least-square refinement by Vogel-Fulcher-Tammann equation:

$$\log \eta = A + \frac{B}{T - T_0}$$



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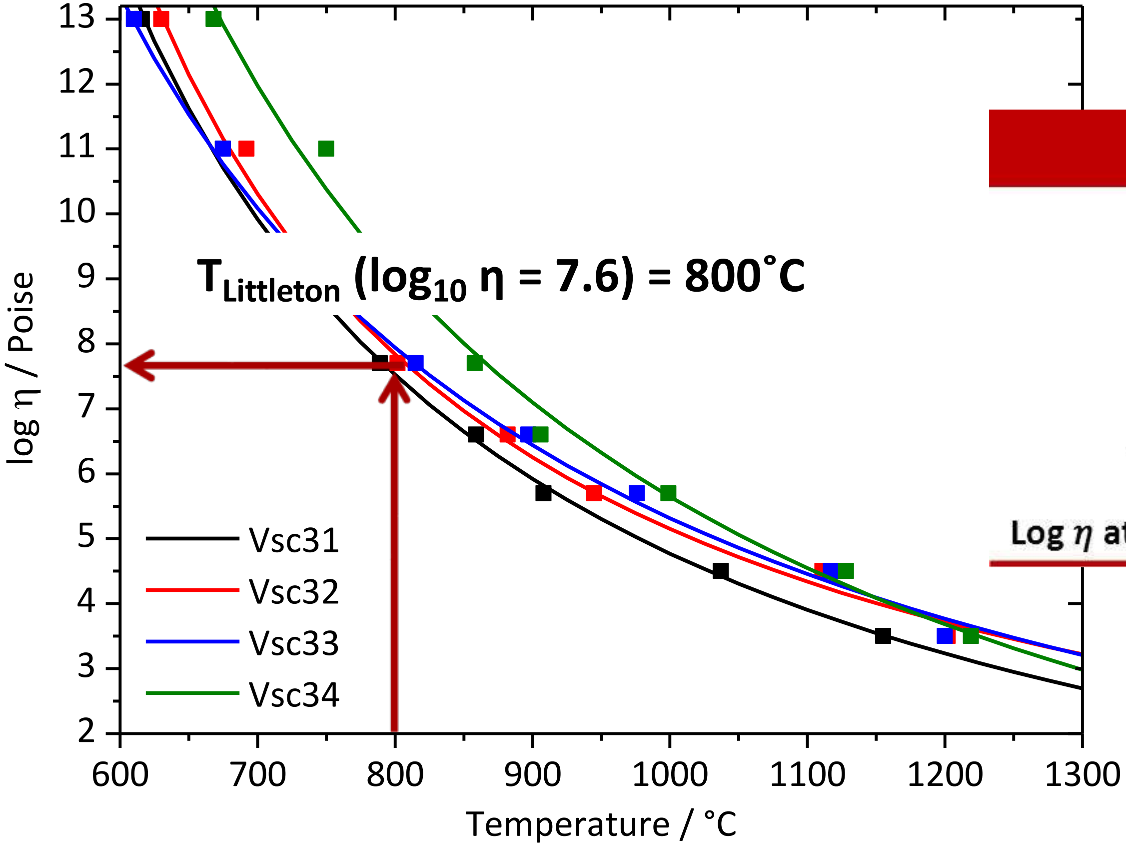

	Vsc31	Vsc32	Vsc33	Vsc34
a	-2.19	-1.00	-2.24	-3.58
b	4917.52	4053.35	5863.19	6809.79
t	293.96	341.80	224.28	262.17
T_L / °C	796	813	820	871
Log η at 900°C / Poise	5.9	6.3	6.4	7.1

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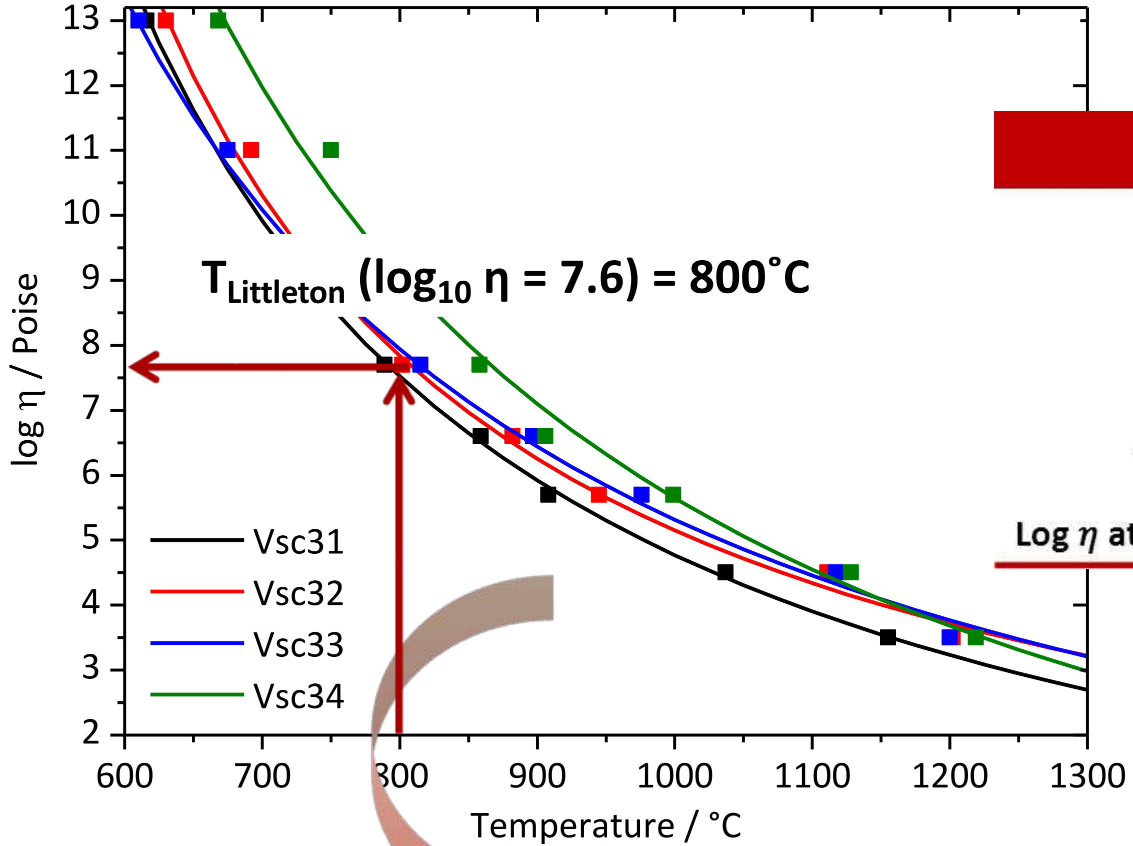

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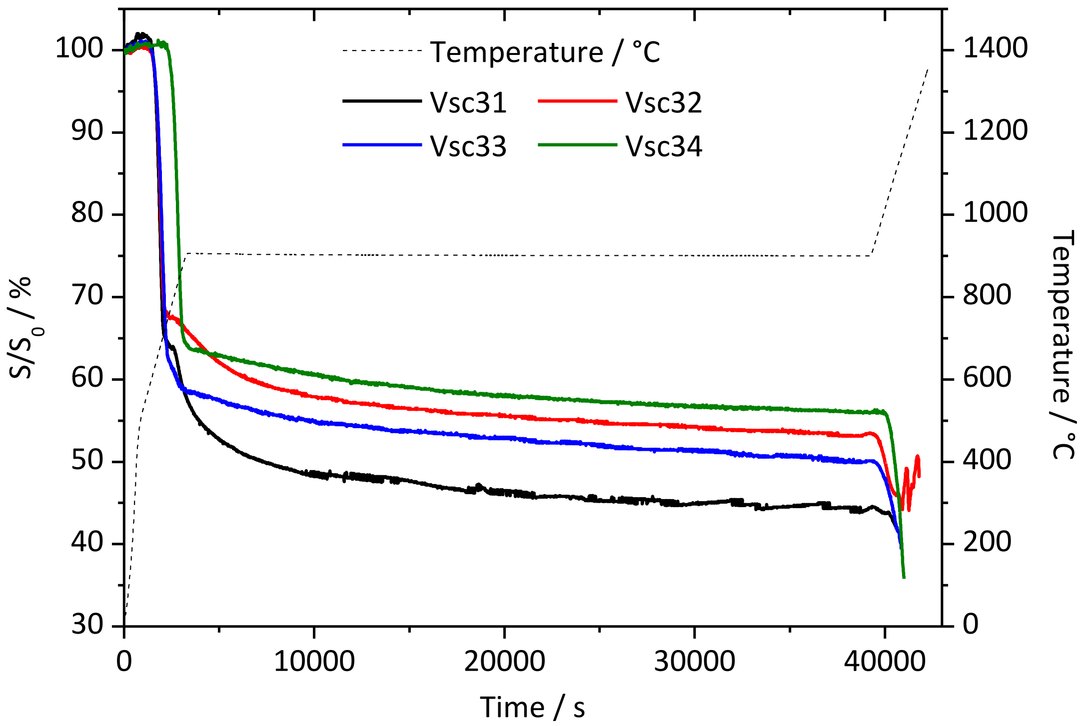
Only Vsc31, Vsc32 and Vsc33 appear suitable

Viscous seal for SOEC

HSM measurements: *wettability*

→ Is the viscosity low enough to allow the seal forming at 900˚C ?
→ Heat treatment: 10h at 900˚C



Glass name and viscosity at 900°C	Initial pellet	Pellet before the plateau at 900°C	Pellet after the plateau
Vsc31 $10^{5.9}$ Poise			
Vsc32 $10^{6.3}$ Poise			
Vsc33 $10^{6.4}$ Poise			
Vsc34 $10^{7.1}$ Poise			

Viscous seal for SOEC

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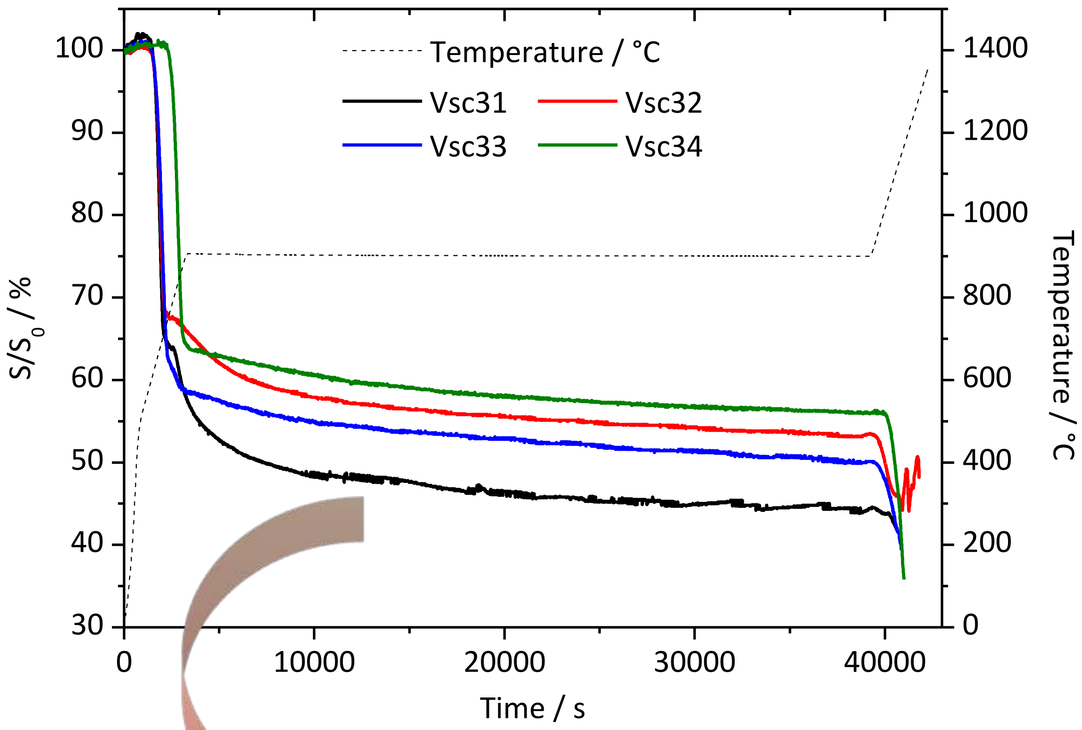

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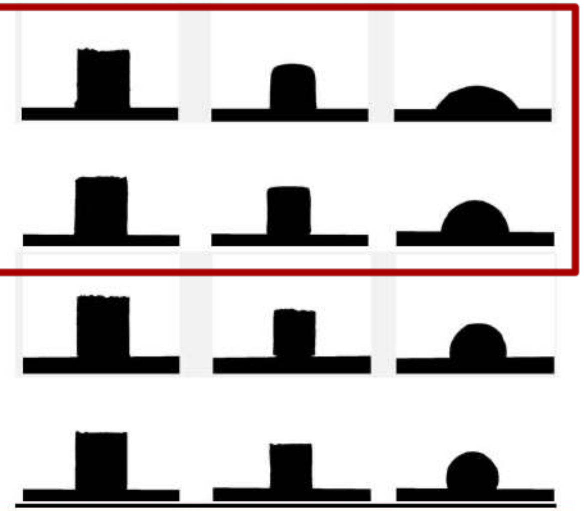
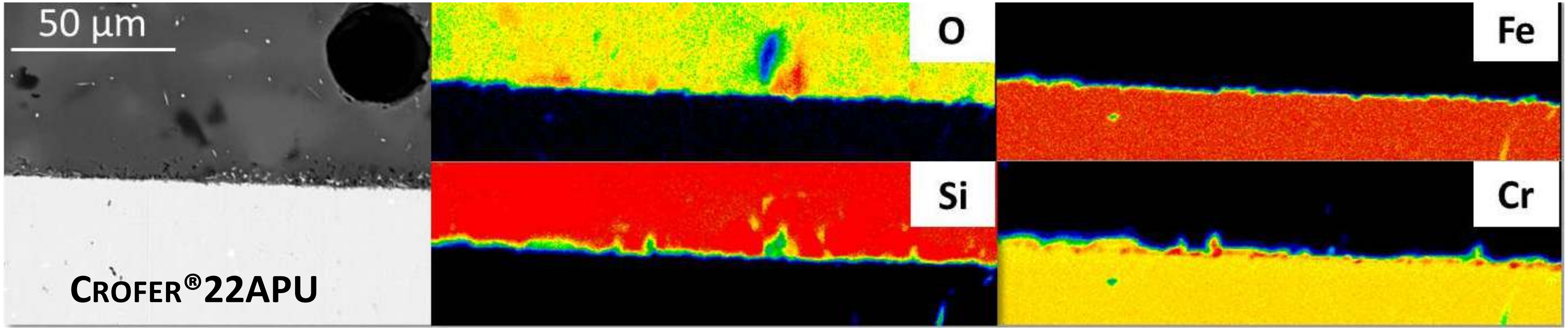


⇒ Seal elaboration: easy at lower viscosity
⇒ Good wettability for Vsc31 and Vsc32 (θ < 90˚)

Viscous seal for SOEC: *stability*

Castaing microprobe observations

Vsc31 ⇒ chromium oxide formation at the interface (1.4 µm)



Viscous seal for SOEC: *stability*

Castaing microprobe observations

Vsc31

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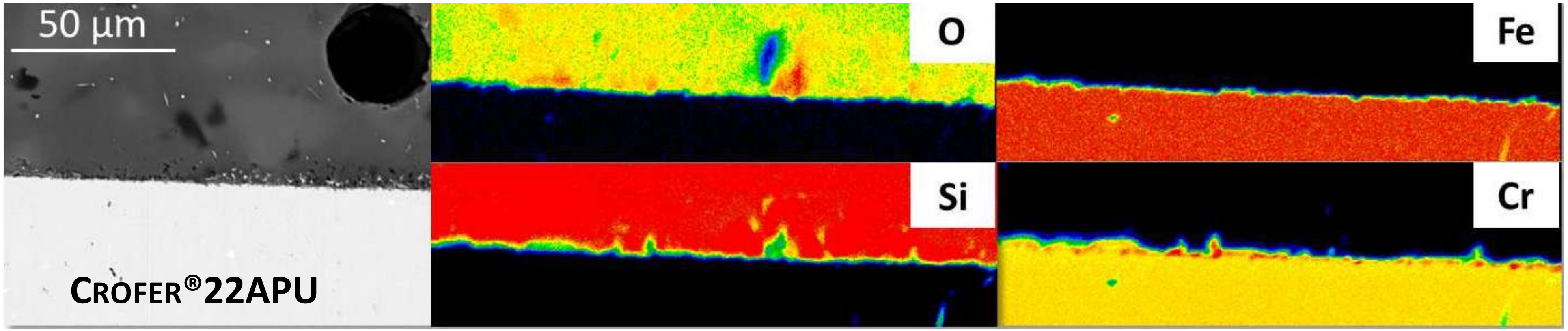
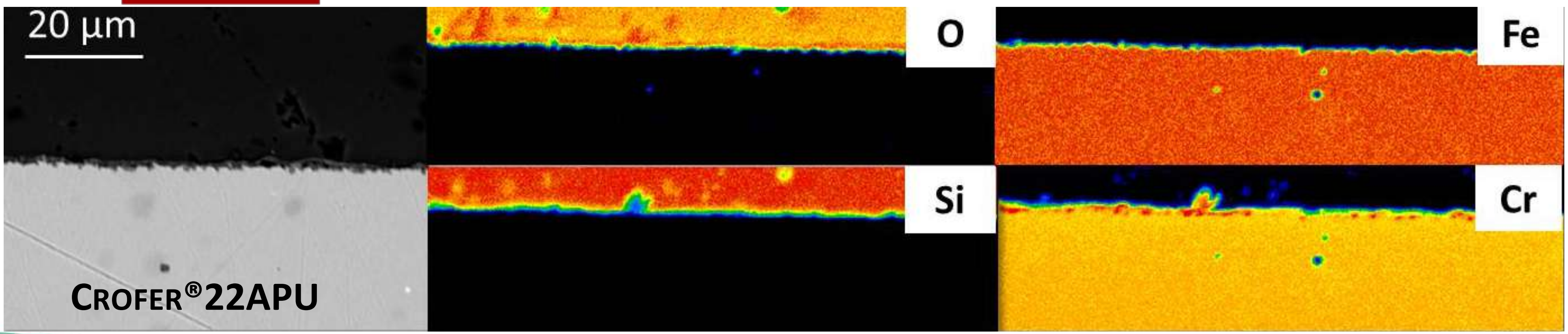


Vsc32

⇒ chromium oxide formation at the interface (1.8 µm)

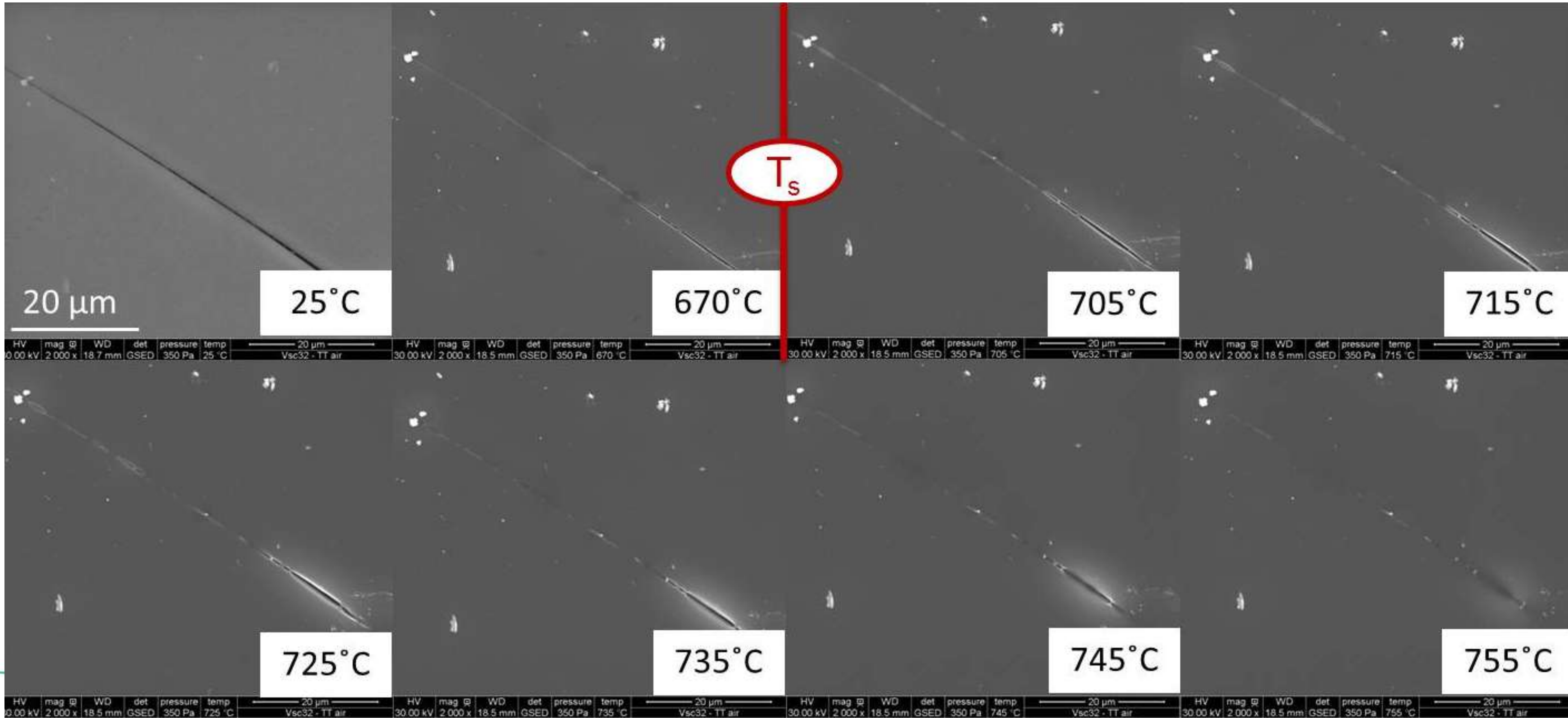


In situ observation of crack healing

In situ observations by HT-ESEM

Vsc32 / Air

	Start of healing	End of healing
Temperature / °C	670	755
Viscosity / Poise	11.05	8.91

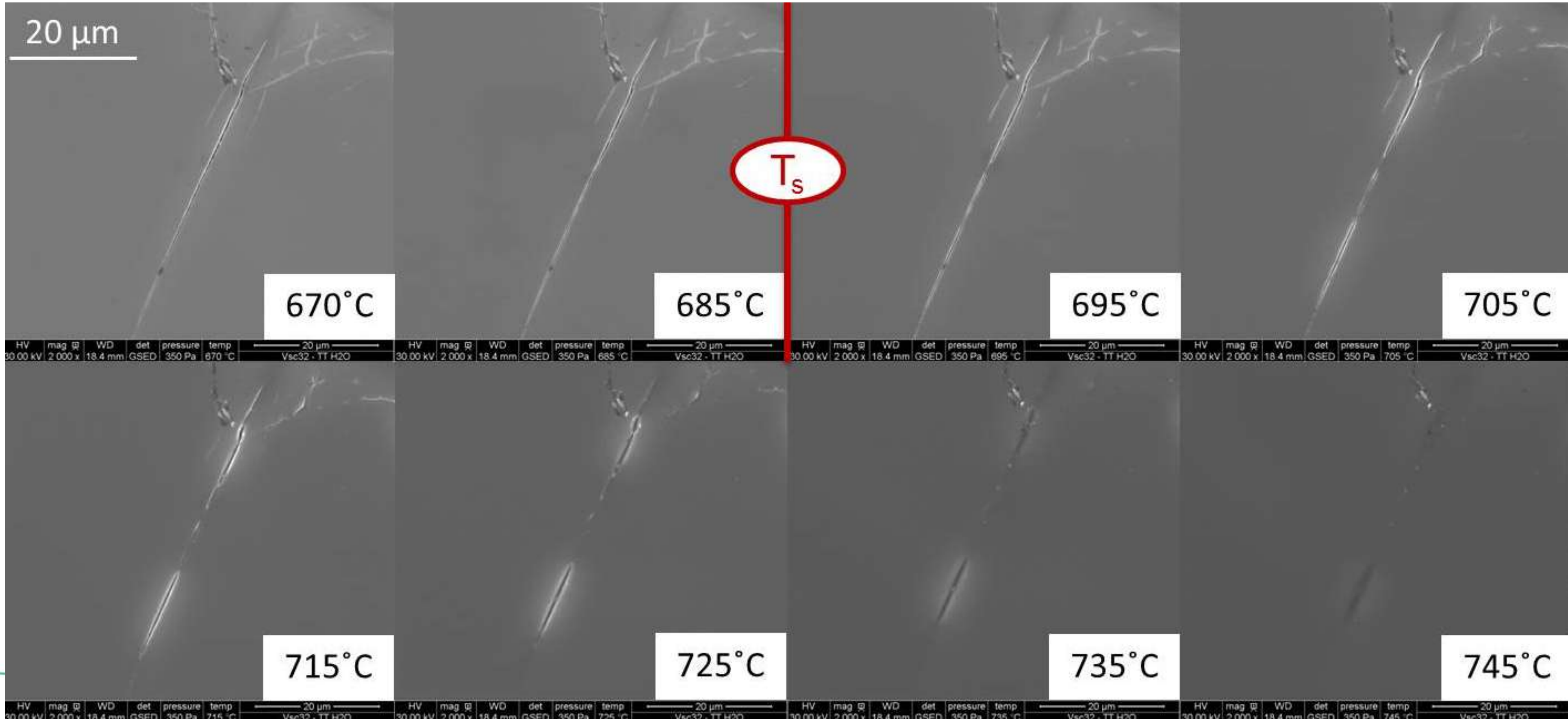


In situ observation of crack healing

In situ observations by HT-ESEM

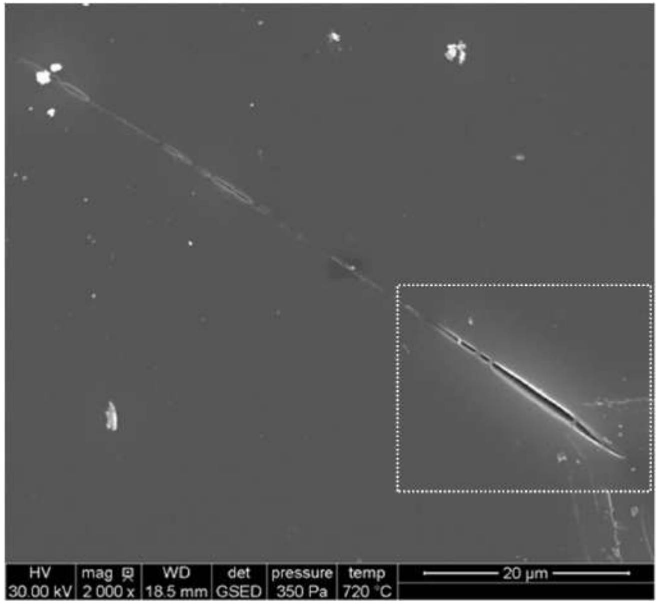
Vsc32 / H_2O

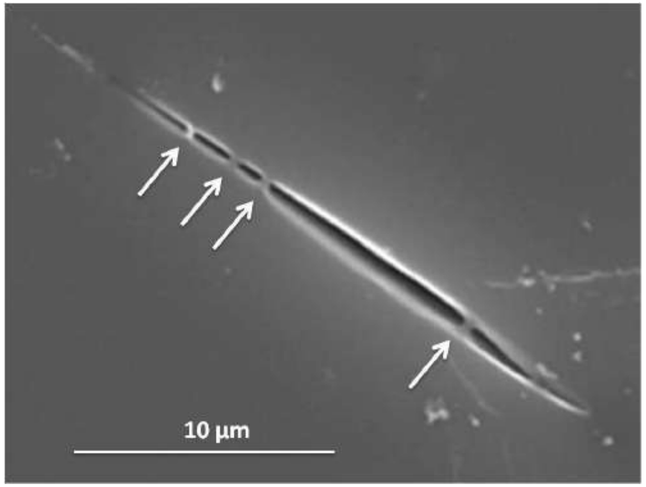
	Start of healing	End of healing
Temperature / °C	670	745
Viscosity / Poise	11.38	9.27



Self-healing theoretical mechanism

⇒ observation of multiple areas of crack pinch-off along the length of the crack





From Méar et al., Taylor & Francis 2011

Self-healing theoretical mechanism

$\Rightarrow$ mathematical model for the description of the kinetics of each stage of the self-healing process. This model allows predicting the time necessary for crack healing, for a given glass composition and operating temperature, using a time coefficient t_c defined as:

$$t_c = K.\eta$$

$\Rightarrow$ where η is the glass viscosity at the healing temperature and K a constant that depends on glass composition, t_c is related to the softening point (T_s)

$\Rightarrow$ time t necessary for healing a crack of length L is expressed as:

$$\ln L = t_c.t$$

From Méar et al., Taylor & Francis 2011

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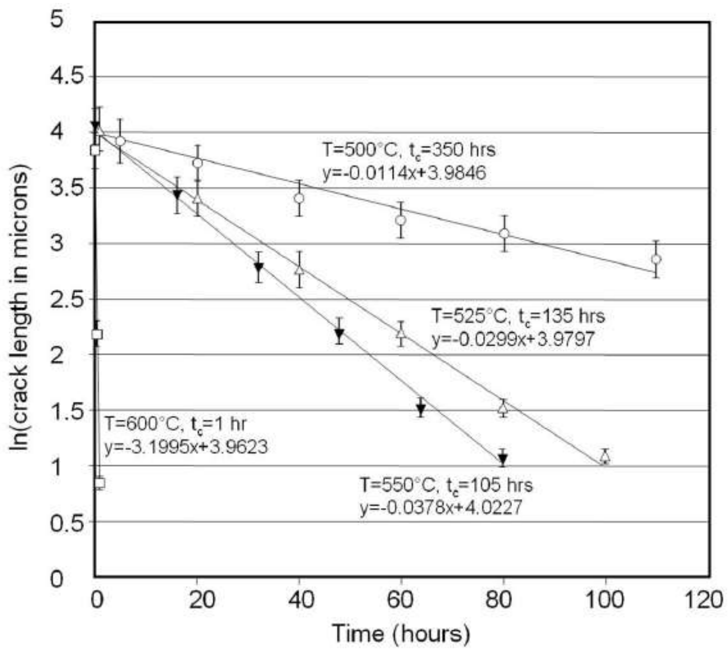
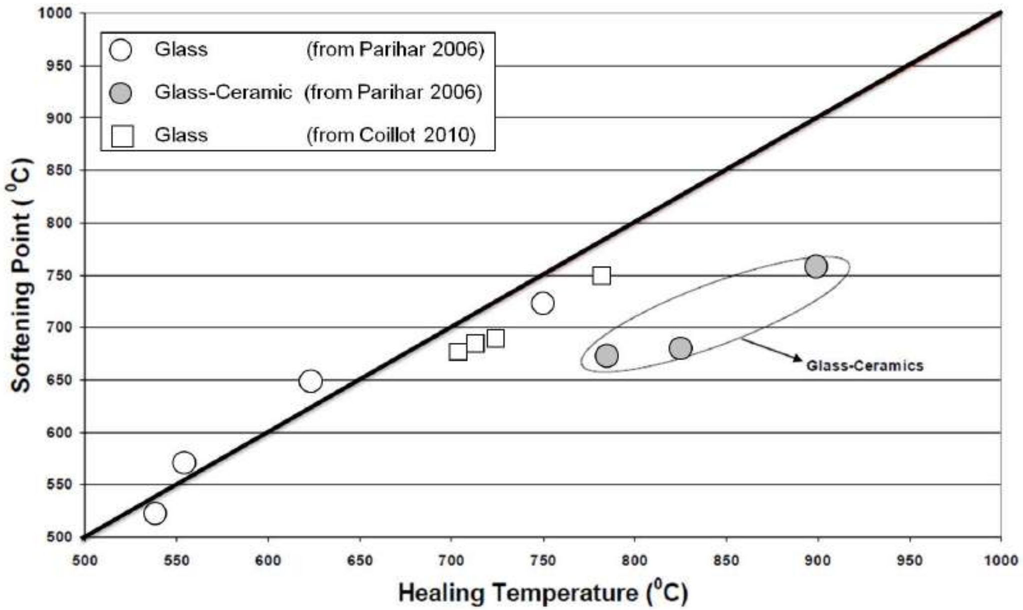


- ➢ healing kinetics strongly depend on healing temperature
- ➢ healing rate is very low when the operating temperature is lower than the softening point

From Méar et al., Taylor & Francis 2011

Self-healing theoretical mechanism



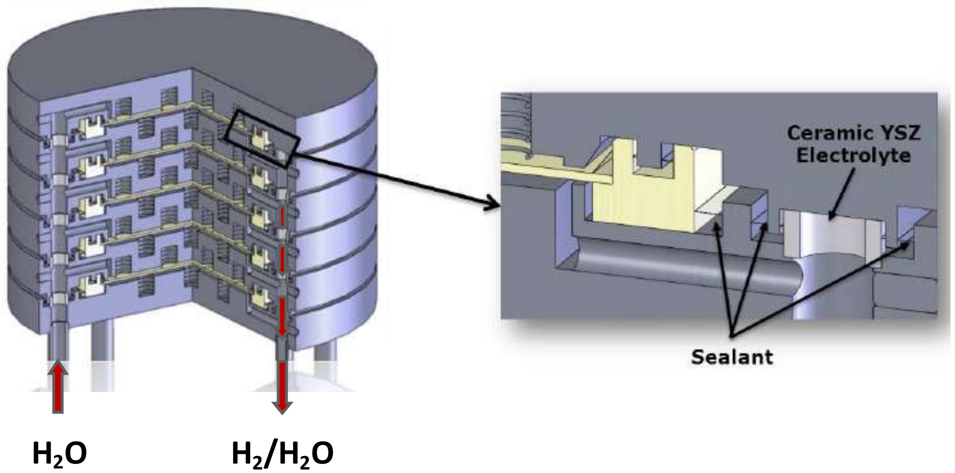
⇒ relationship between softening temperature and healing temperatures

⇒ sets of data reported, concordant and yield to the conclusion that the healing temperature of glasses is very close to the softening temperature

⇒ self-healing can be obtained over a large range of temperatures, depending on glass composition

From Méar et al., Taylor & Francis 2011

Leak test of Vsc32 glass



Schematic representation of a SOEC stack. Insert is highlighting interconnections ceramic-ceramic and ceramic-metal

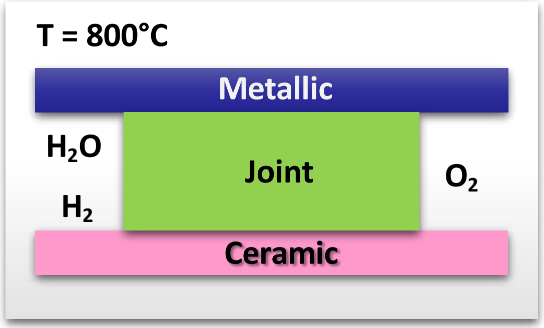
Requirements

- Operating temperature : **800°C**
- T_{max} acceptable : ≈ **900°C**
- Working pressure : **300 mbar → 3 bars**
- Atmospheres : **O_2 and H_2/H_2O**
- Materials : different thermal expansion coefficients

  Metals : α_{20-700} = **14.8×10^{-6} K^{-1}** (Haynes)

  α_{20-700} = **11.2×10^{-6} K^{-1}** (Crofer)

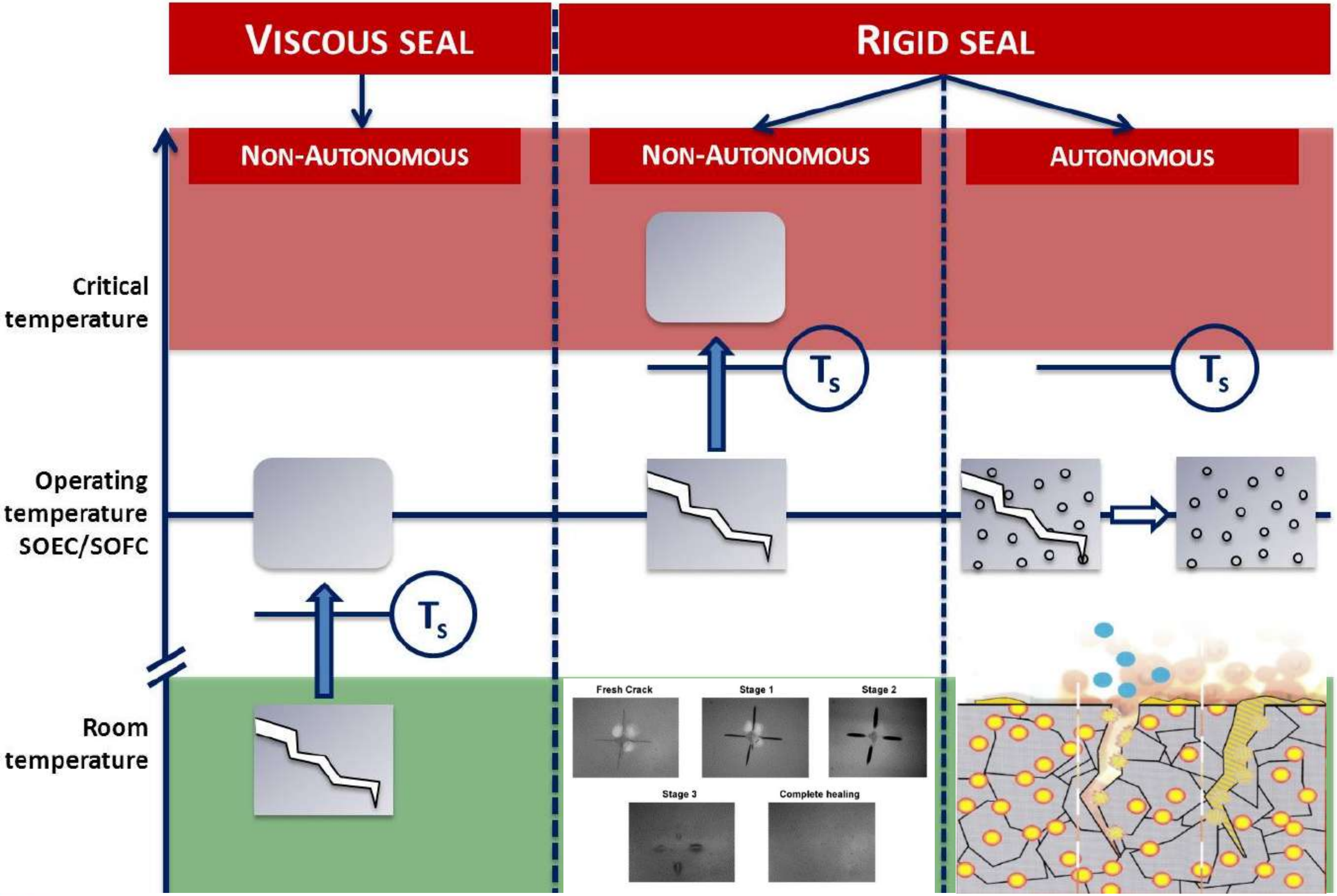
  Ceramics: α_{20-700} = **10.8×10^{-6} K^{-1}** (YSZ)
- Leak rate : **10^{-3} $Pa.m^3.s^{-1}$**



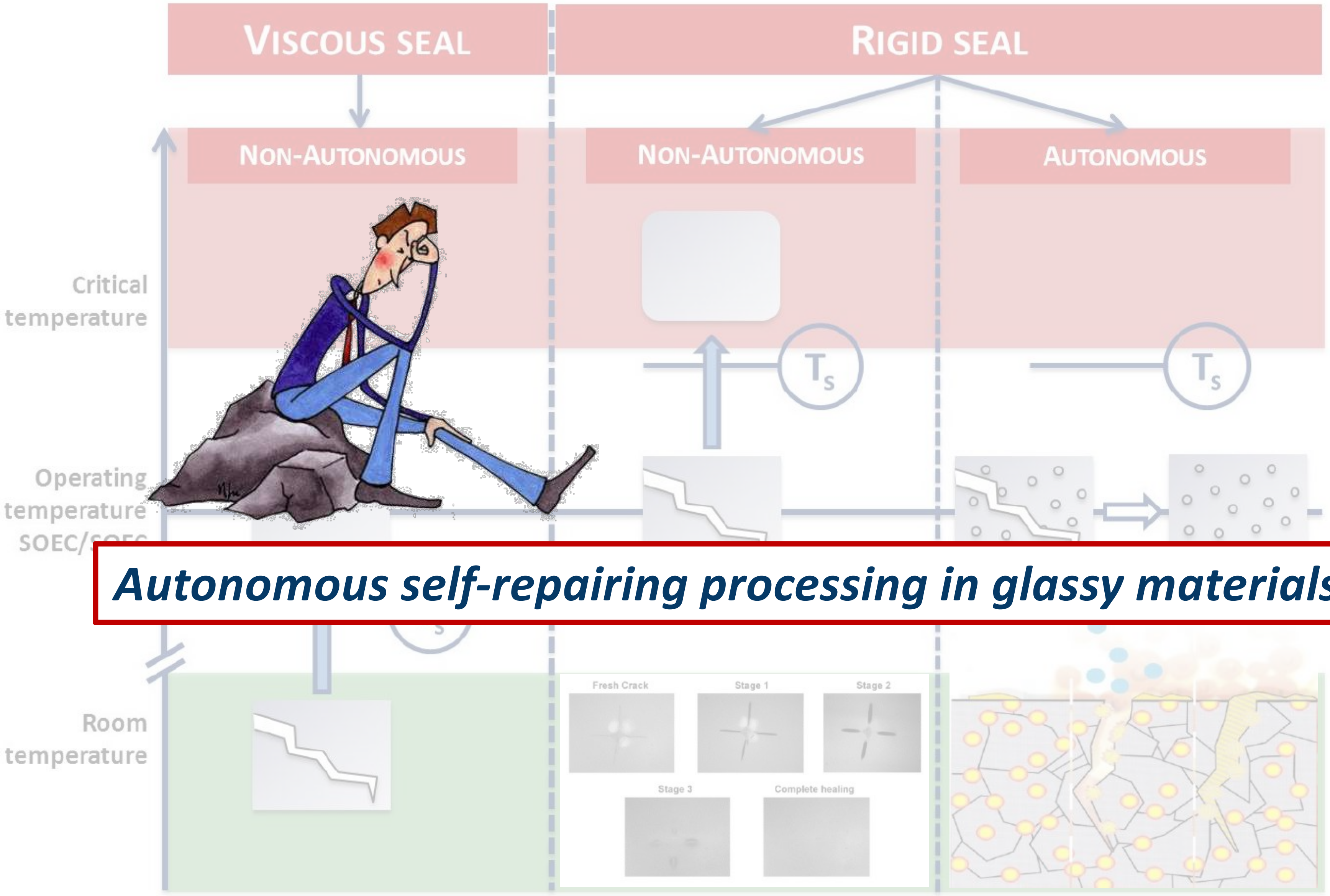
The production of high quality hermetic seals is essential to the long-term performance and reliability of SOECs

From Coillot et al., Int. J. Hydrogen. Energy 2012

Self-healing glassy materials: *concept*



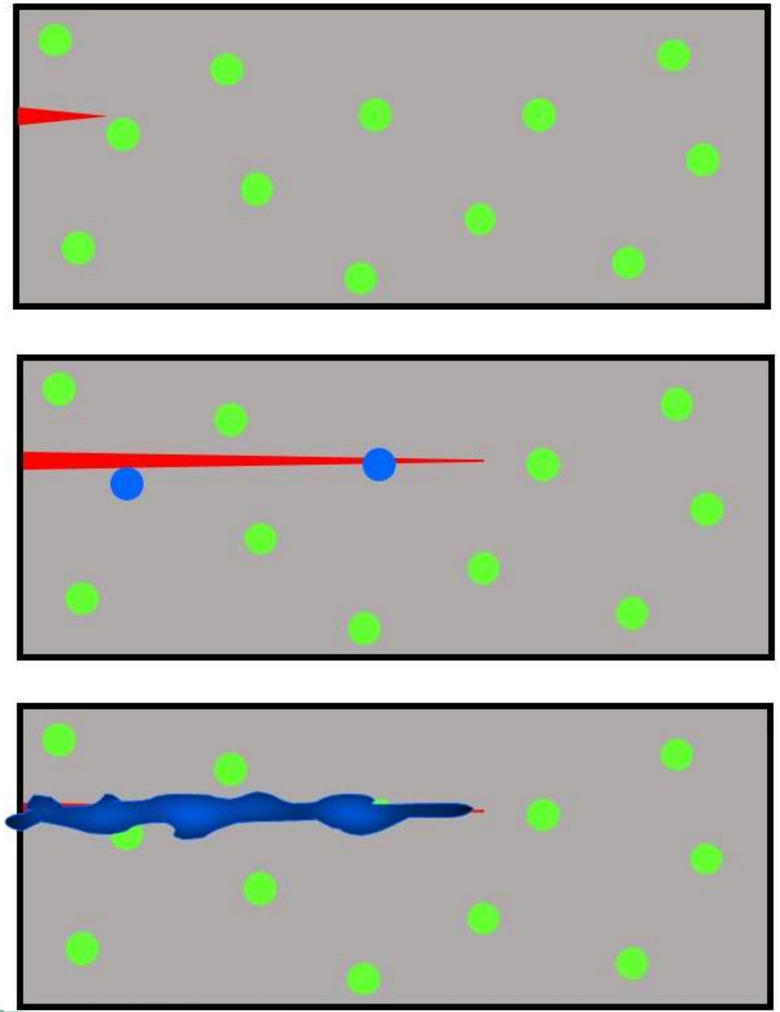
Self-healing glassy materials: *concept*



Autonomous self-repairing processing in glassy materials ?

Autonomous self-healing glassy materials

Autonomous self-healing glass matrix upon occurrence of cracks



→ **Crack formation into the composite during operation**

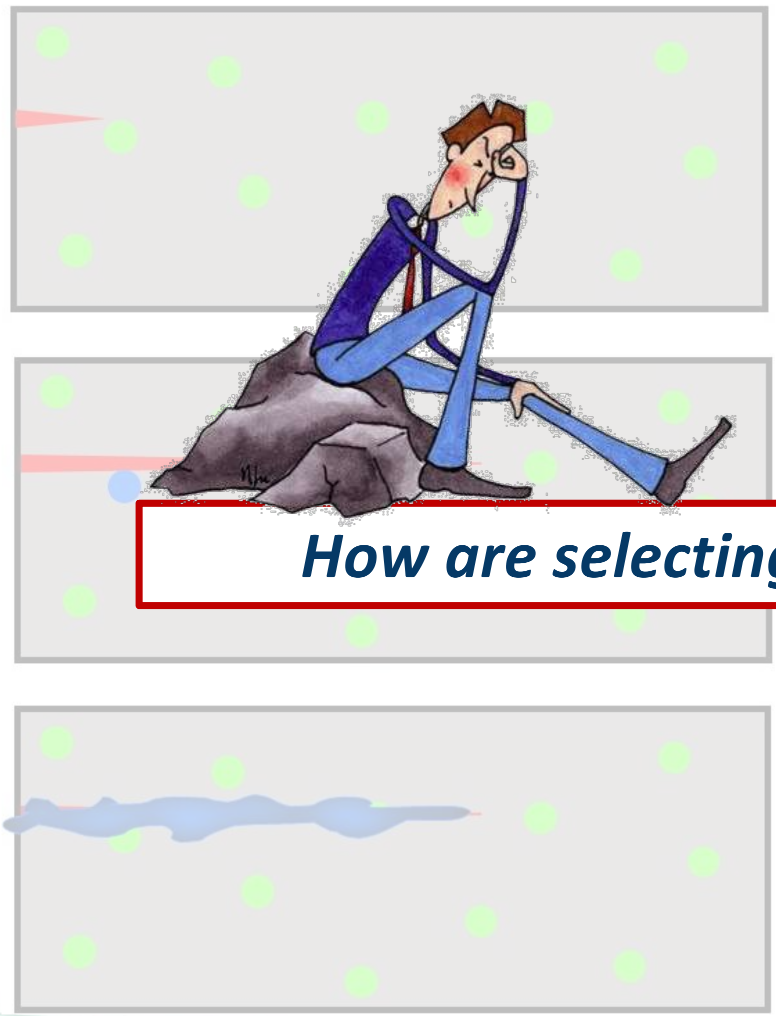
→ **Contact of O_2 contained into atmosphere with some active particles leading to their oxidation**

→ **Formation of fluid oxides capable to flow into the crack and to fill it**

From Coillot et al., Patent WO 2010/136721 A1

Autonomous self-healing glassy materials

Autonomous self-healing glass matrix upon occurrence of cracks



→ Crack formation into the composite during operation

→ Contact of O_2 contained into atmosphere with some active particles leading to their

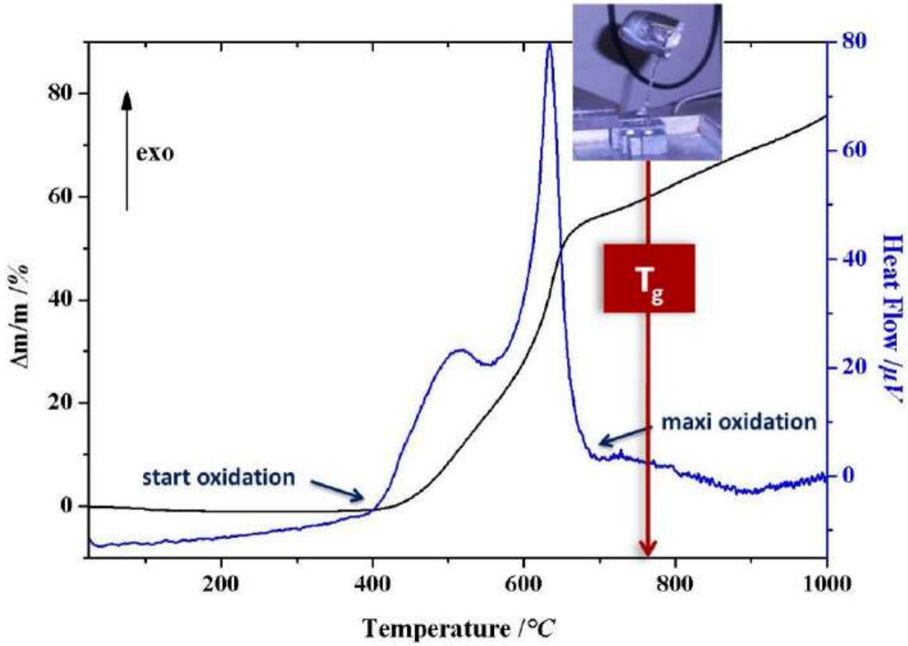
How are selecting the healing particles ?

→ Formation of fluid oxides capable to flow into the crack and to fill it

From Coillot et al., Patent WO 2010/136721 A1

Healing agent selectivity: *VB*

Differential thermal analysis



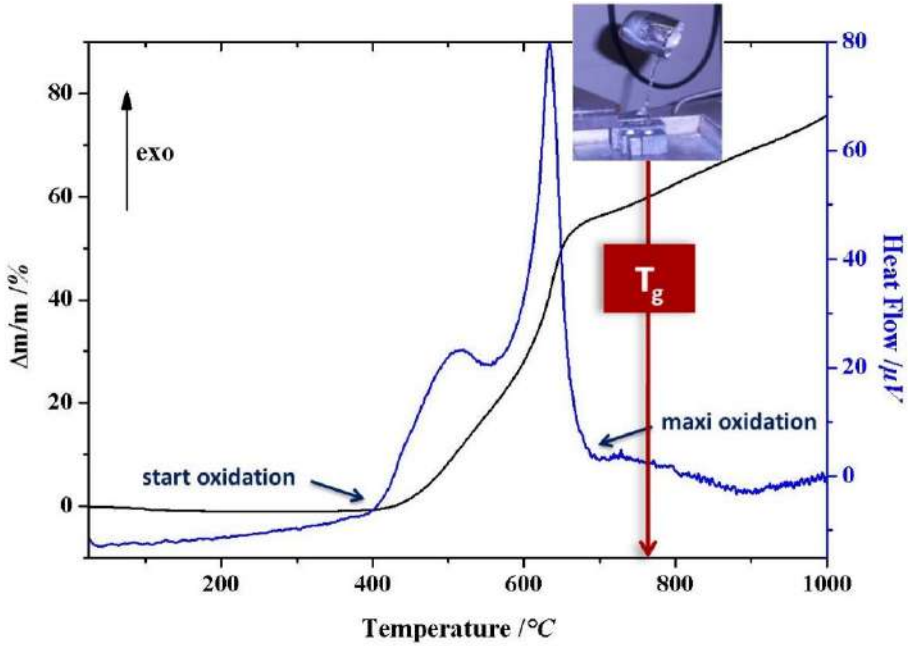
→ stable at working temperature in the absence of air

→ oxidize rapidly in the presence of air

→ oxides must be fluid at the working temperature

Healing agent selectivity: *VB*

Differential thermal analysis



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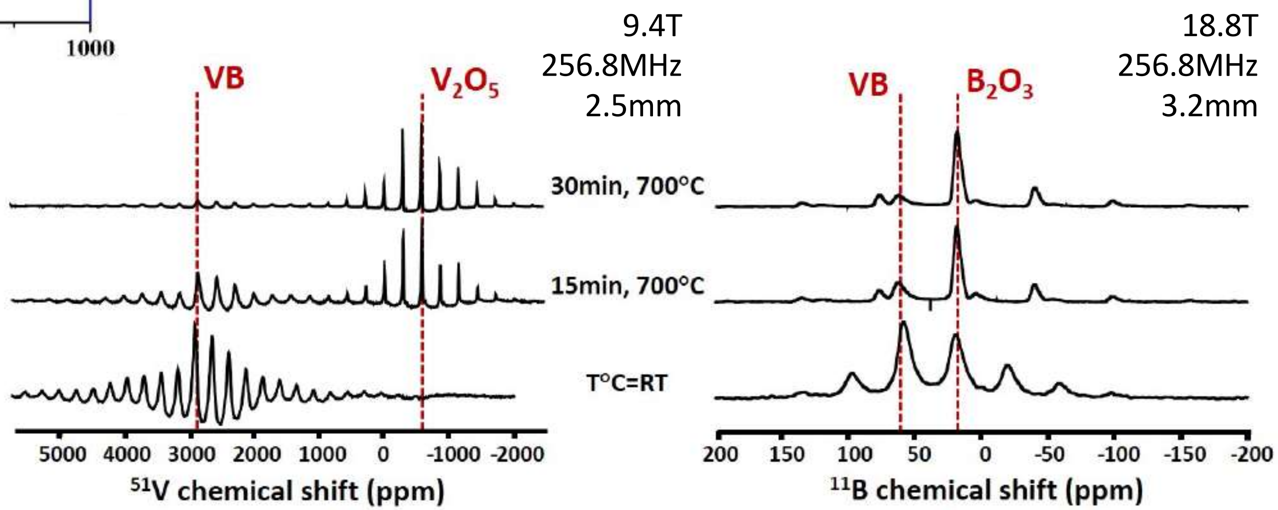
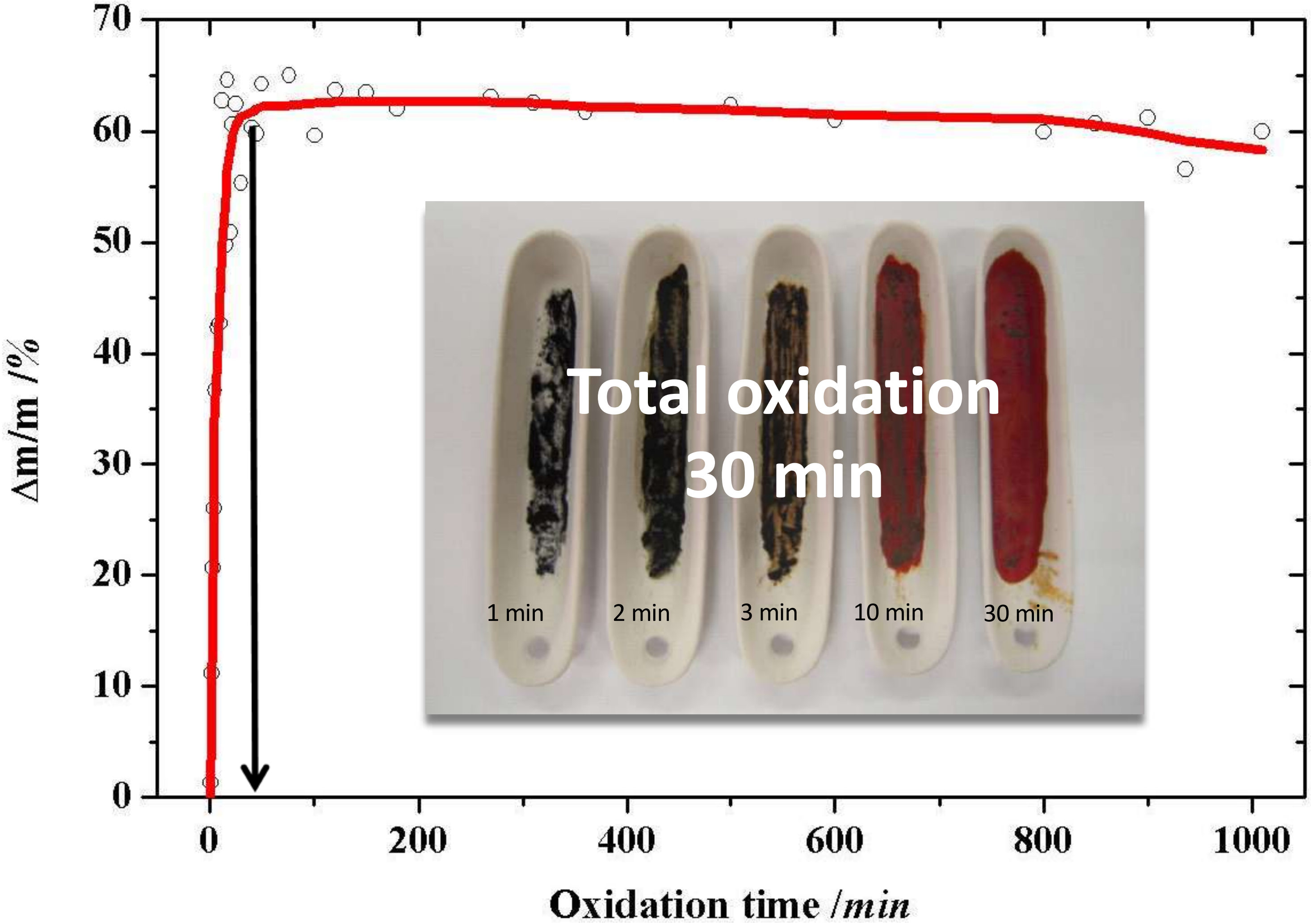
Nuclear magnetic resonance

$2VB + 4O_2 \rightarrow V_2O_5 + B_2O_3$

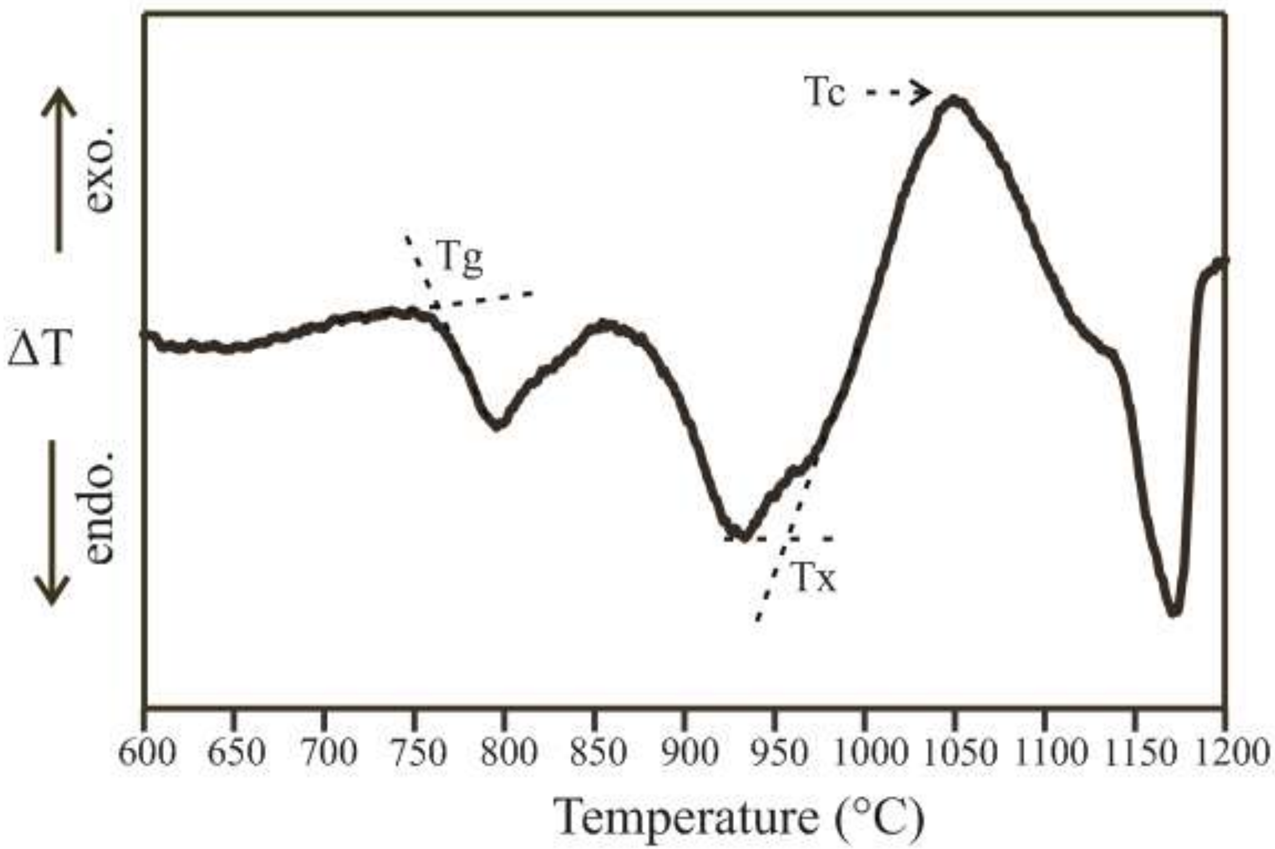


Healing agent selectivity: *VB*



Glass thermal analysis: *DTA*

Sealing glass composition: 28.6 BaO – 14.3 CaO – 9.5 Al_2O_3 – 47.6 SiO_2



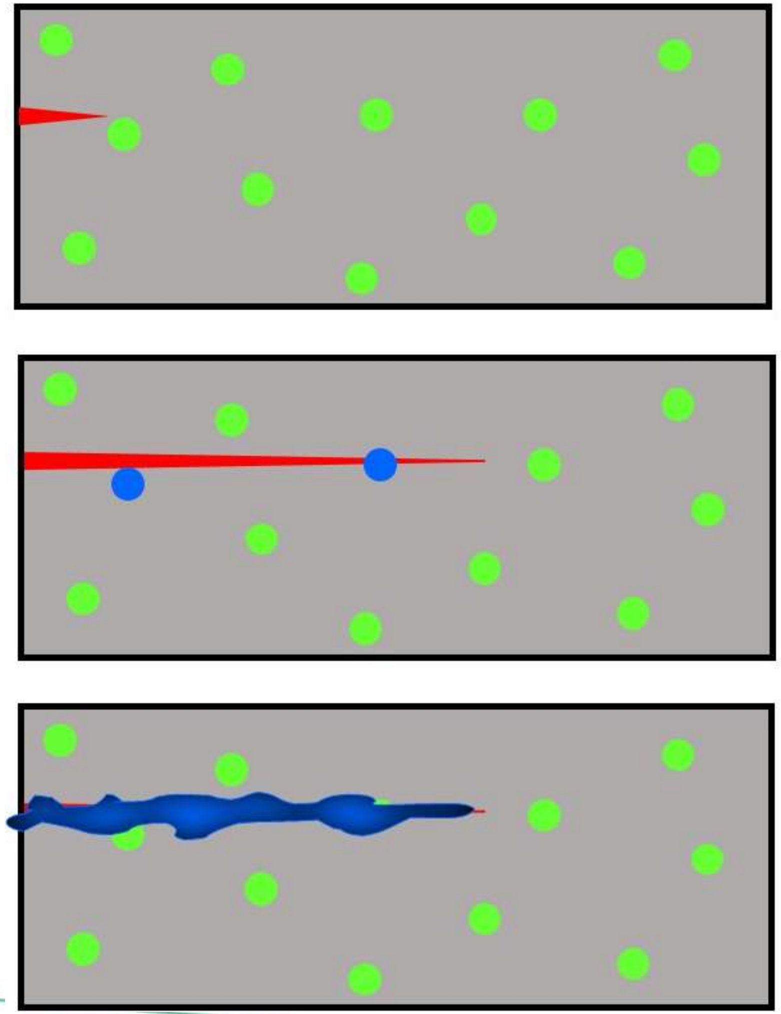
Tg=750°C

Tx=970°C

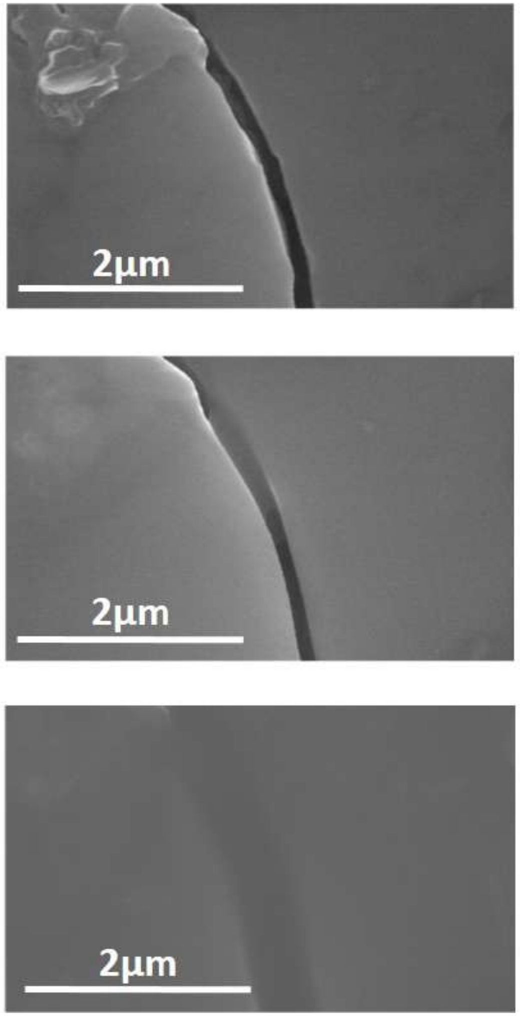
Tc=1070°C

In situ observation of crack healing

Autonomous self-healing glass matrix upon occurrence of cracks



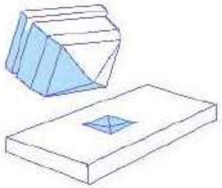
2D *in situ* observation by environmental microscopy (at 700°C in air)



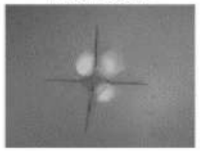
In situ observation of crack healing

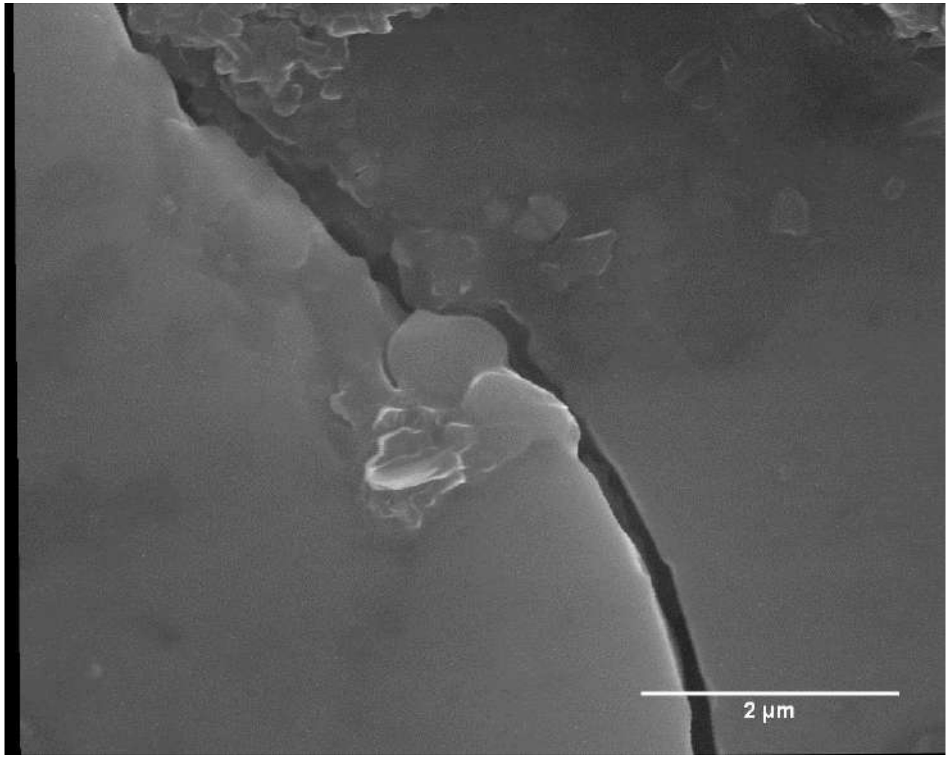
Environmental microscopy (HT-ESEM)

Conditions: 700˚C, P_{O2} = 450Pa



Fresh Crack





Isothermal treatment at 700˚C in air:

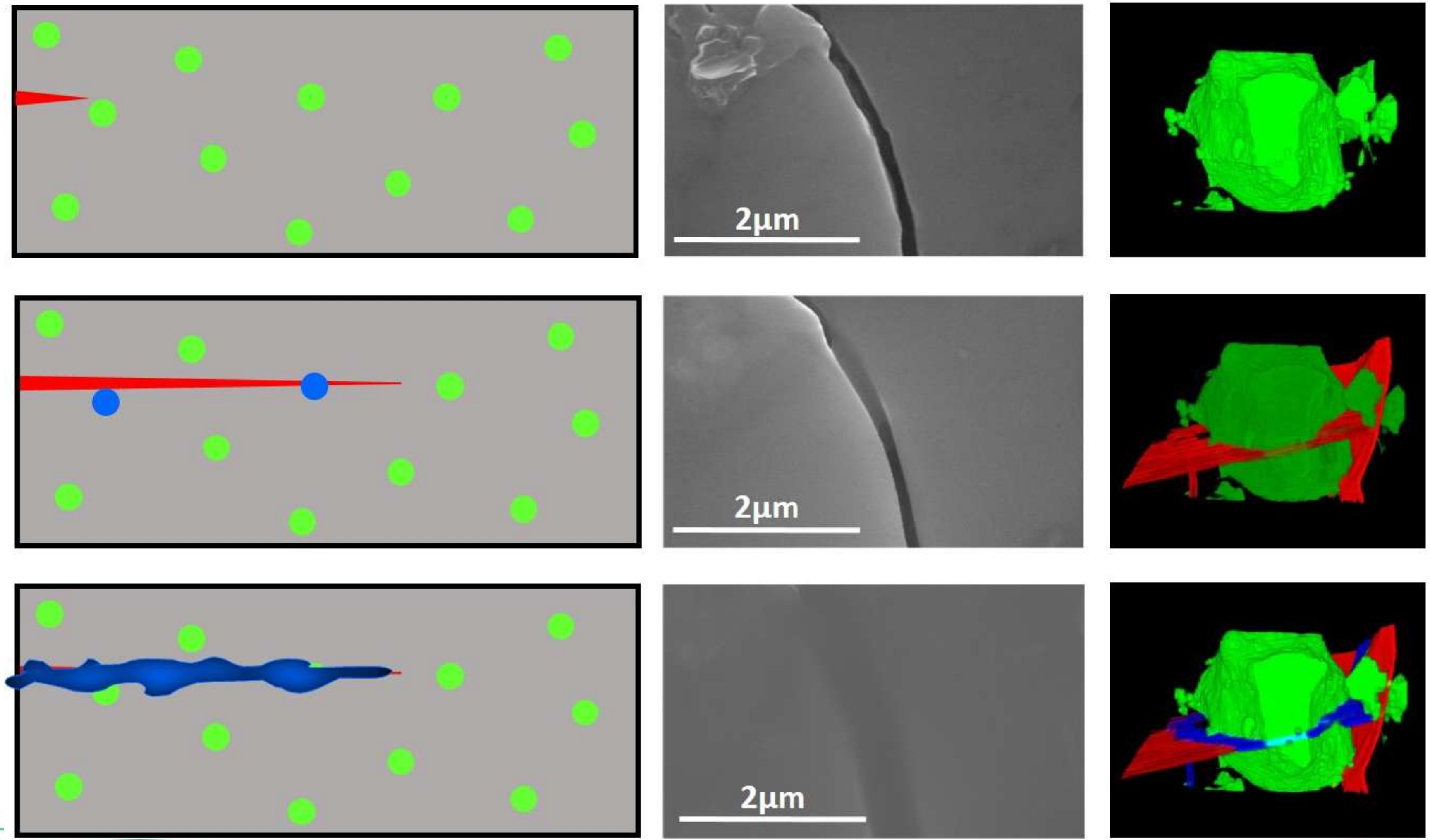
→ oxidation of VB particles and formation of V_2O_5 and B_2O_3

Ex situ observation of crack healing

Autonomous self-healing glass matrix upon occurrence of cracks

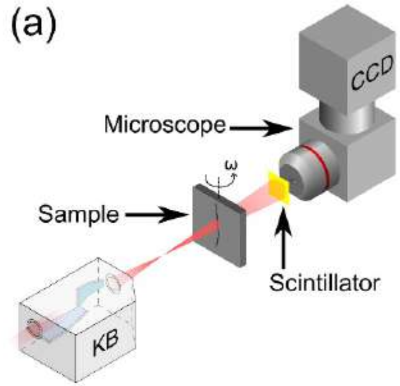
2D *in situ* observation by environmental microscopy (at 700°C in air)

3D observation by nano-tomography (ID22, ESRF)

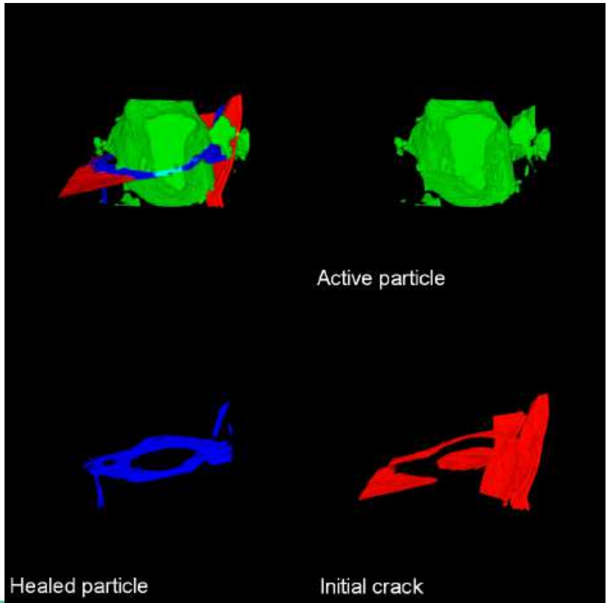


Ex situ observation of crack healing

X-ray nano-imaging (ID22NI)



X-ray nano-tomography image reconstitution of a crack throughout the material



Ex situ observation of crack healing

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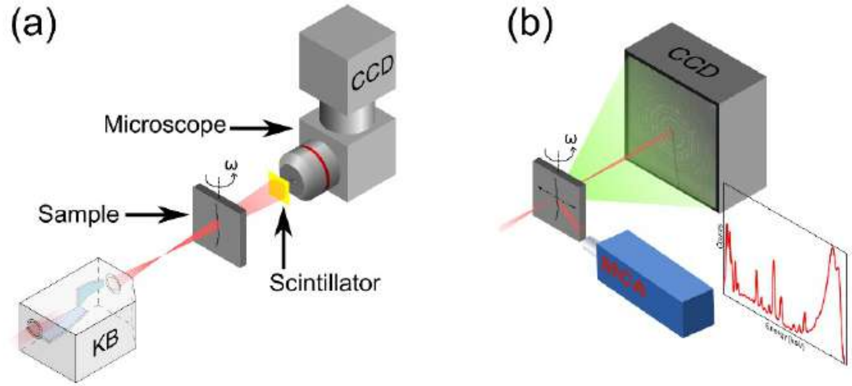

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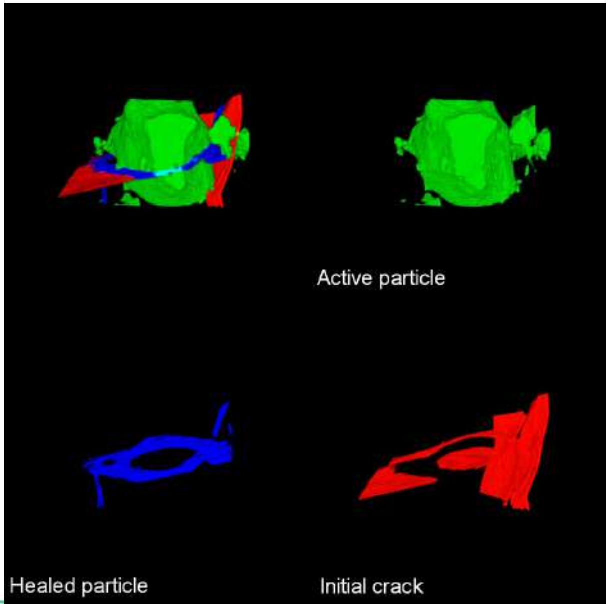
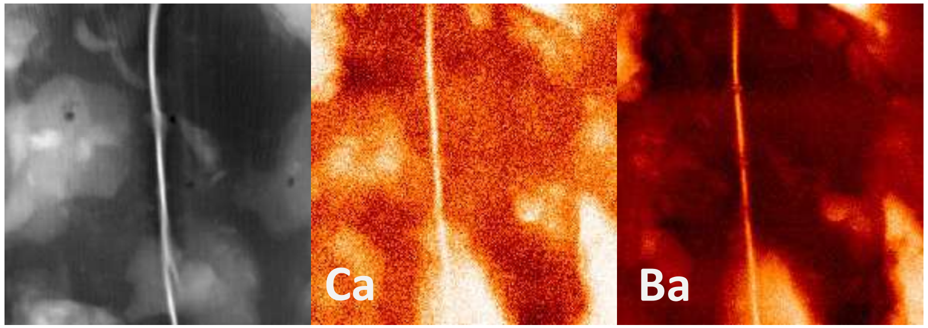
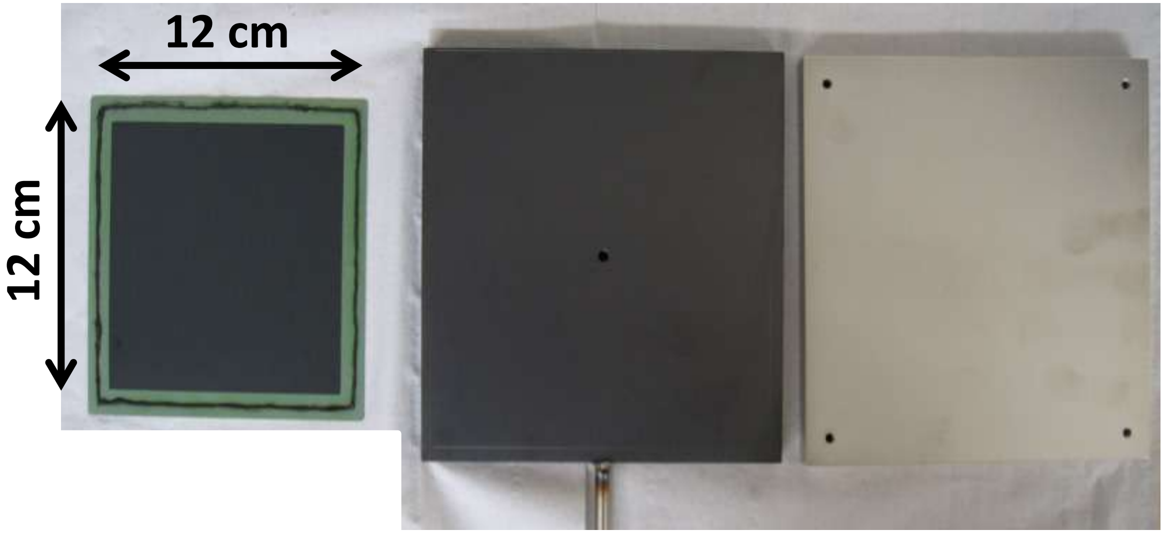


X-ray fluorescence 2D mapping of calcium and barium repartition in a crack area



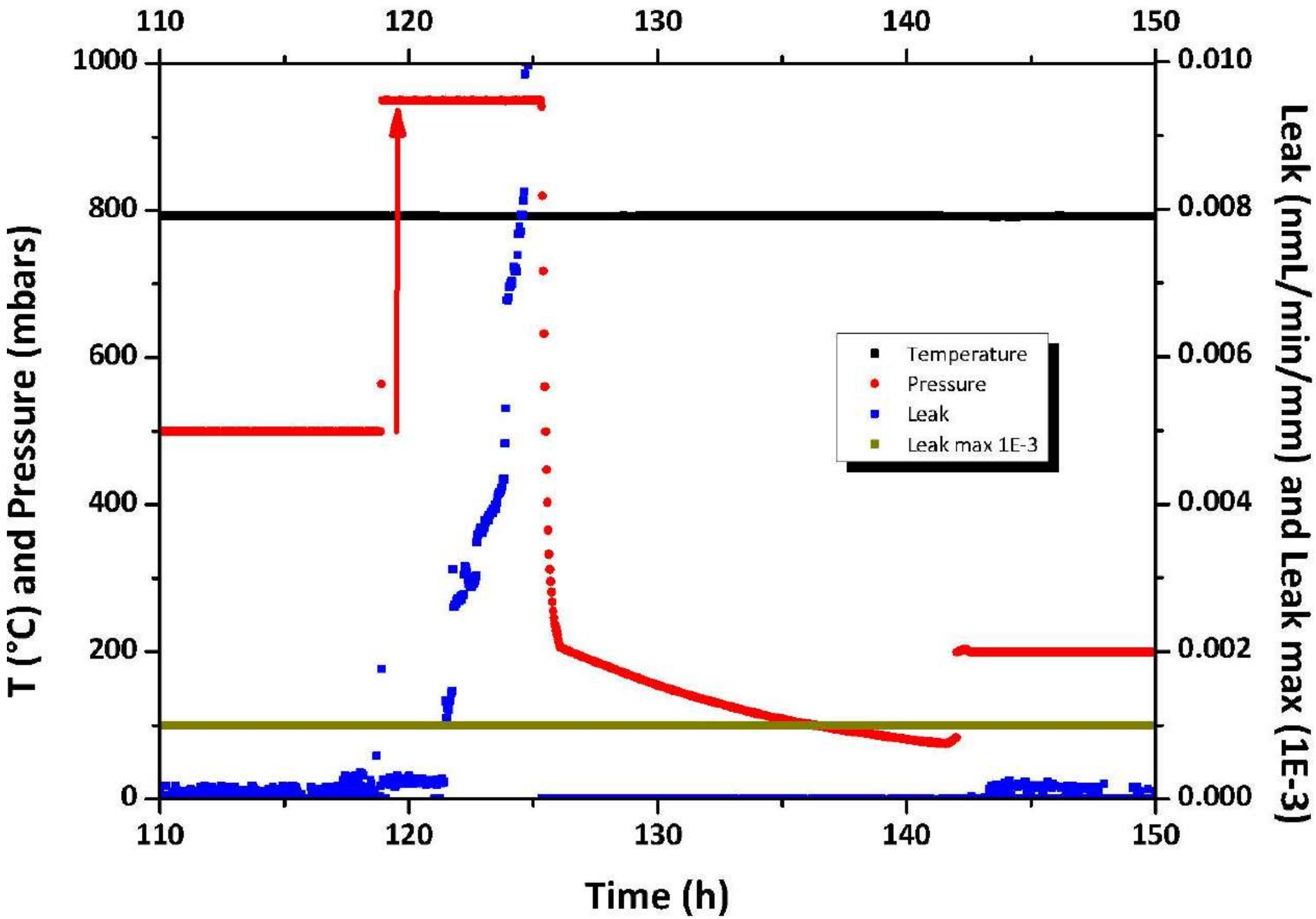
Leak test: *experimental device*



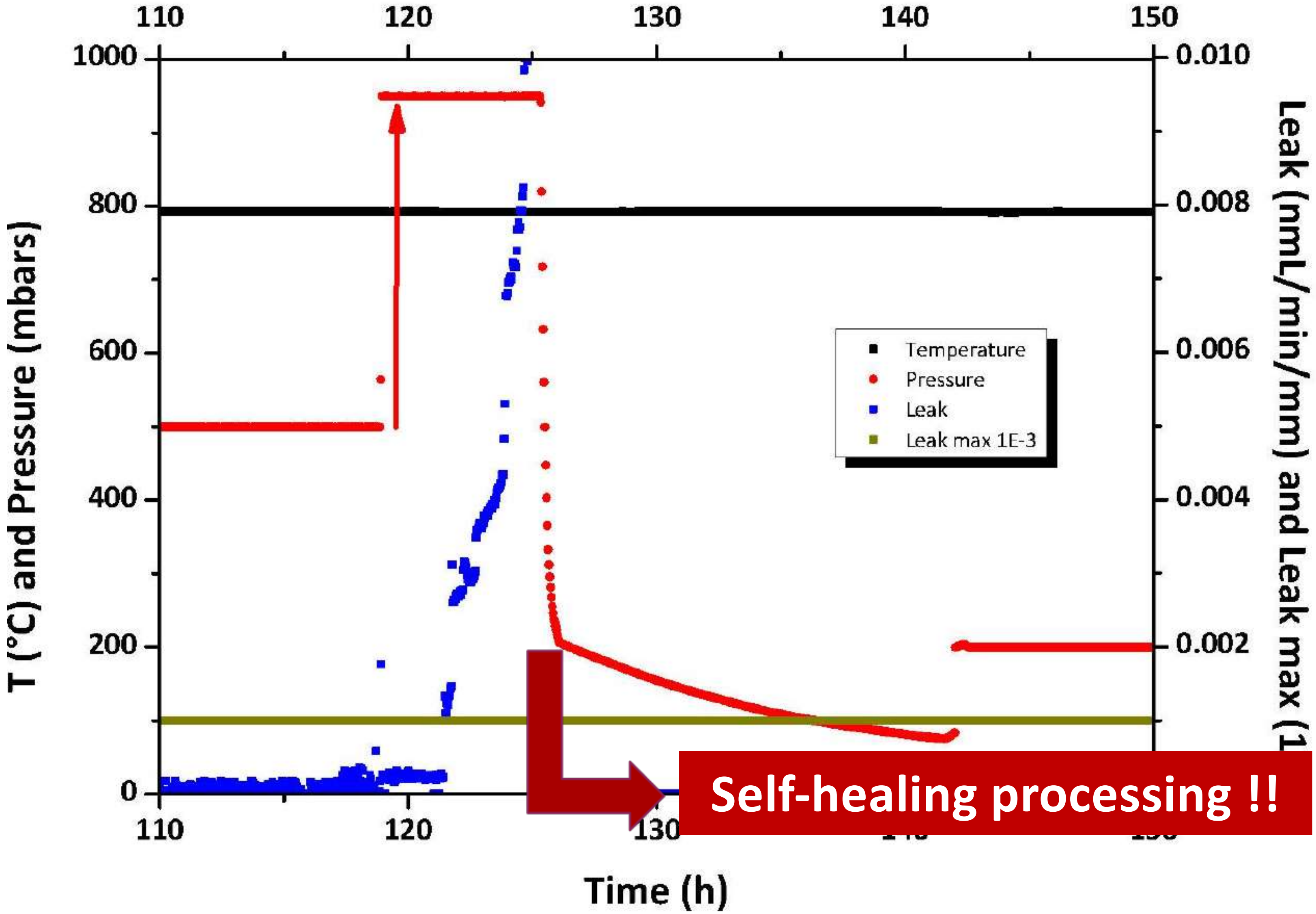
Maxi weight supported by the oven : 50 kg

Maxi pressure : 340 mbars

Self-healing efficiency test



Self-healing efficiency test



Summary

✓ Development of self-healing glassy material concept at macro-scale for high temperature applications

✓ Synthesis and physico-chemical characterization of glassy matrix for fuel cell

✓ Self-healing is an option to increase materials lifetime

→ *Application*: glassy-ceramic sealing for SOEC / SOFC

Les projets ciblés du PEPR-H2

Production d'hydrogène	Stockage de l'hydrogène	Conversion de l'hydrogène
		
CELCER-EHT : Cellules Céramiques EHT durables, performantes et bas coûts	**SOLHyd** : Stockage solide de l'hydrogène: nouvelles stratégies, nouveaux matériaux	**FLEXISOC**: Flexibilité des cellules SOC vis-à-vis du combustible
PROTEC : Développement de cellules d'électrolyse à base de céramiques à conduction protonique	**HYPERTSTOCK**: Stockage hyperbare de l'hydrogène: référentiel et méthodologies matériaux	**PEMFC95**: Développement d'une cellule de PEMFC capable de fonctionner durablement à 95°C
		DURASYS-PAC: Durabilité et Résilience des Systèmes Piles à Combustible

CELCER-EHT

PROJET CELCER-EHT	Cellules Céramiques EHT durables, performantes et bas coût	
Coordonné par	CEA-LITEN (Florence LEFEBVRE-JOUD)	Durée 6 ans

Moyens prévus	Permanents : 38 chercheurs académiques et 20 ingénieurs-chercheurs CEA 13 doctorants et 18 postdoc 11 laboratoires académiques + CEA

THANK YOU FOR YOUR KIND ATTENTION

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