3rd SumGlass – 09/29/2023 – Nîmes

Self-healing glassy sealant for SOFC/SOEC technology

François O. MÉAR

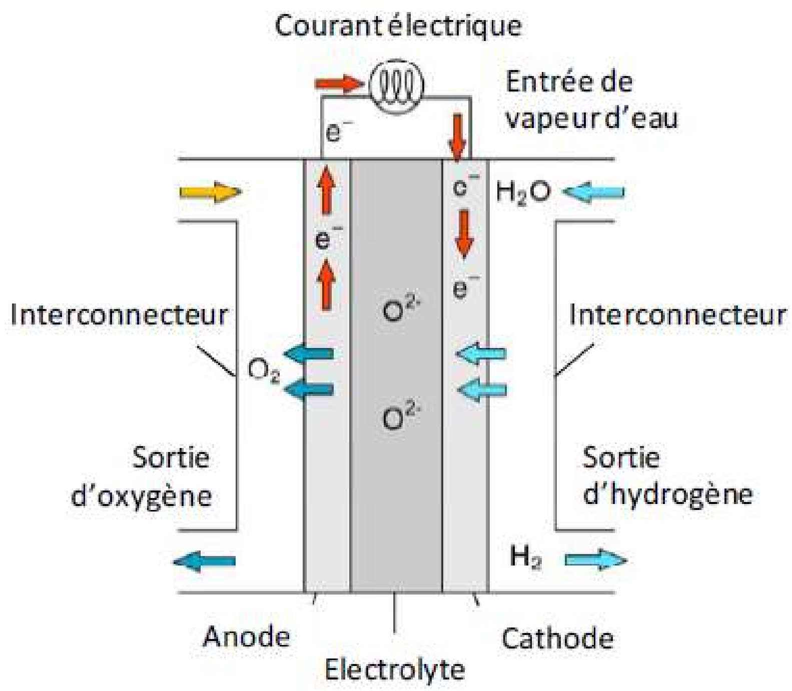
PhD: Daniel COILLOT (ULille), Sandra CASTANIÉ (DGA),
Lionel MONTAGNE (ULille), Renaud PODOR (CEA-ICSM)

Outline

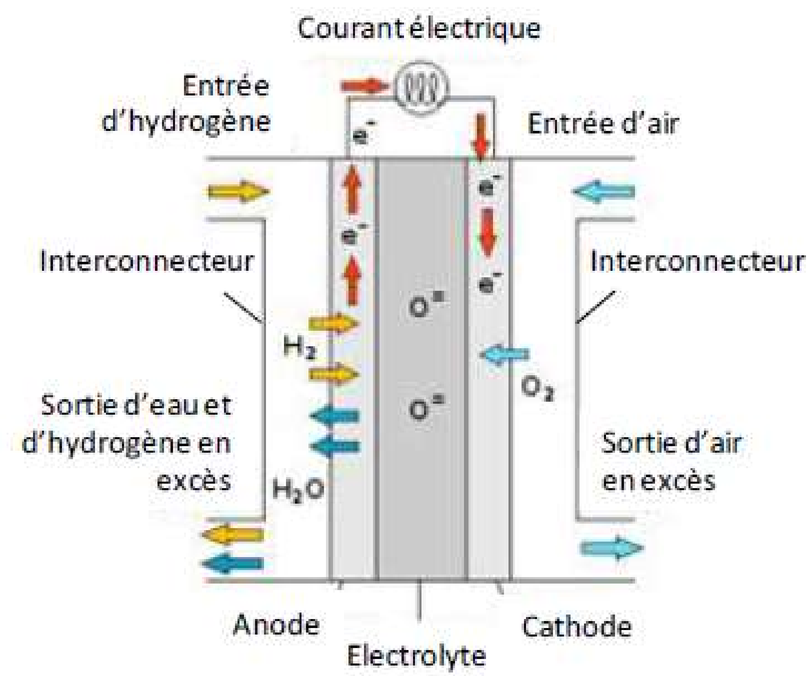
- ✓ **SOFC/SOEC technology**
- ✓ **Glass-sealant for SOFC/SOEC technology: state of the art**
- ✓ **Self-healing: background – definition**
- ✓ **Non-autonomous & autonomous self-healing concepts**
- ✓ ***Application*: self-healing in glassy sealant**
  - ✓ **Non-autonomous self-healing processing in viscous seal**
  - ✓ **Autonomous self-healing concept for rigid seal**
- ✓ **Conclusions**

SOEC vs SOFC technology

Solid Oxide Electrolysis Cell (SOEC)



Solid Oxide Fuel Cell (SOFC)



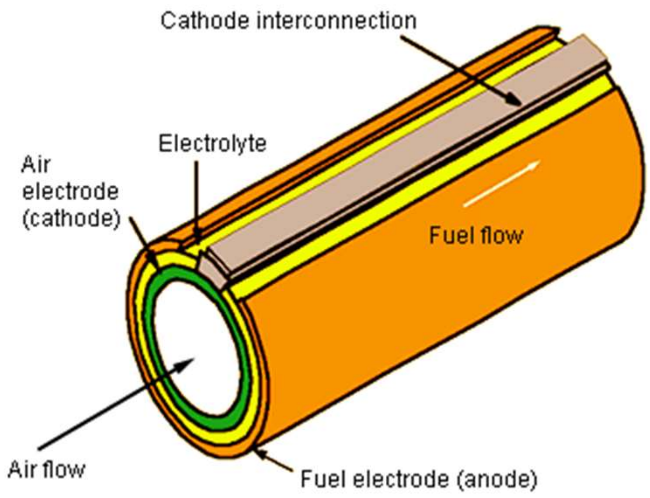
Cathode reaction: $H_2O + 2\ e^- \rightarrow H_2 + O^{2-}$

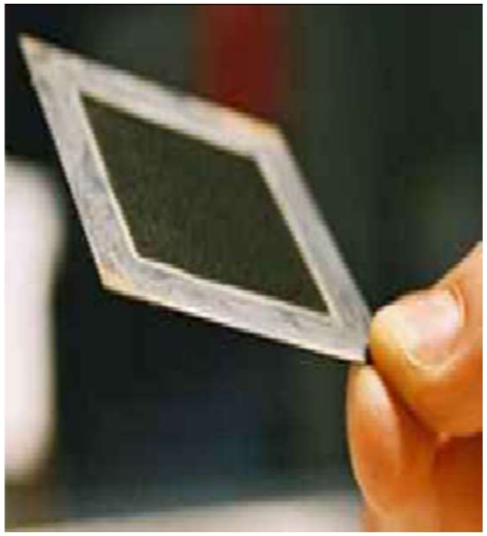
Anode reaction: $O^{2-} \rightarrow \frac{1}{2}\ O_2 + 2\ e^-$

Cathode reaction: $\frac{1}{2}\ O_2 + 2\ e^- \rightarrow O^{2-}$

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

SOFC technology





Tubular Siemens-Westinghouse

Planar Global

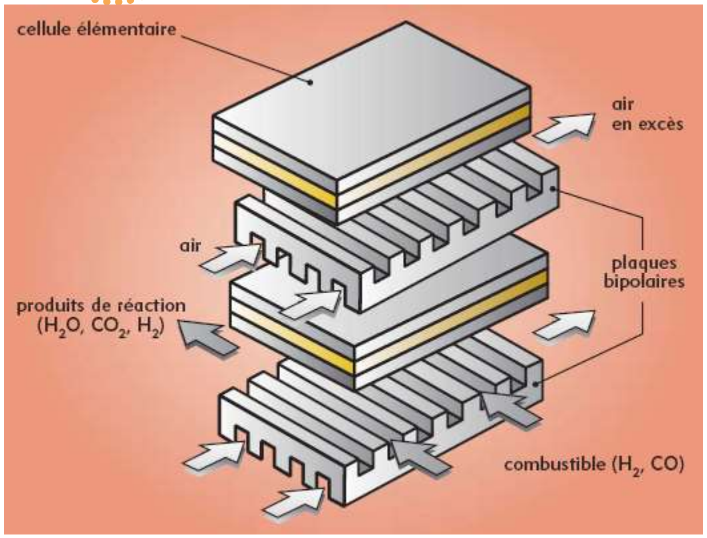
Metal supported thin film
Ceres Power

HT-SOFC
1000°C

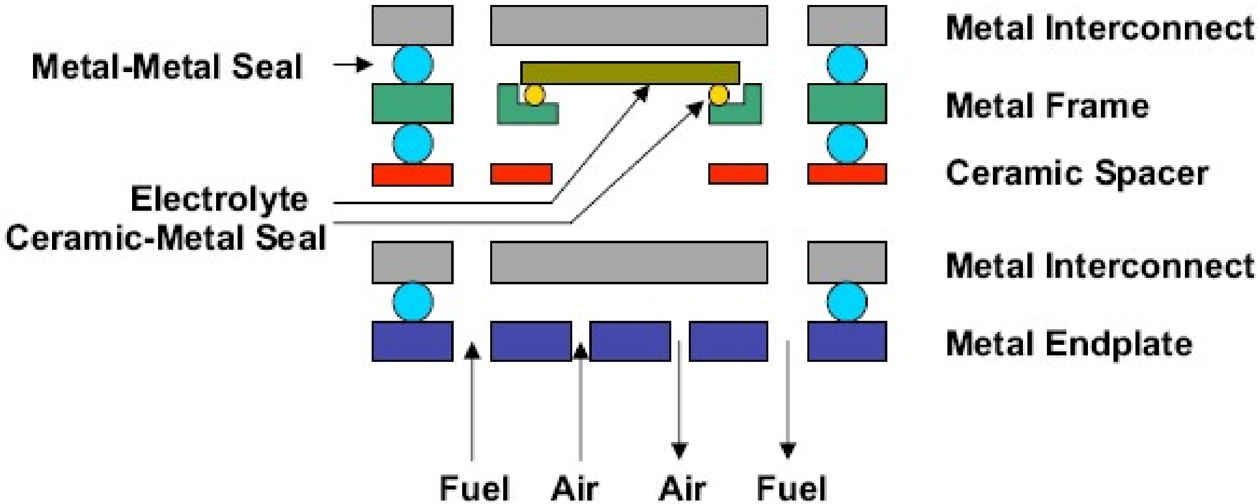
Advantages sealing durability

IT-SOFC
550°C

Glassy sealant for SOFC technology



Fuel cell design by Jüllich (Germany)



Requirements of a SOFC/SOEC seal

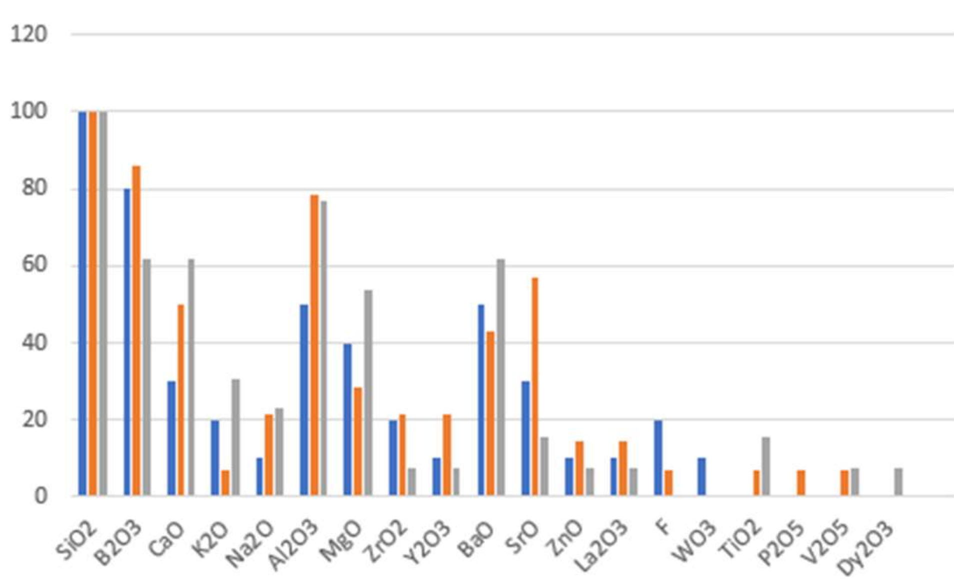
Properties	Requirements
Thermal properties	- **Thermal expansion coefficient at 9.5 – 12.0 × 10^{-6} °C^{-1}** - Thermally stable ~ 5,000h for mobile applications and for ~ 50,000h for stationary applications at 650-900°C cell operating temperatures
Chemical properties	- Resistant to vaporization and 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 and disadvantages of different types of seals

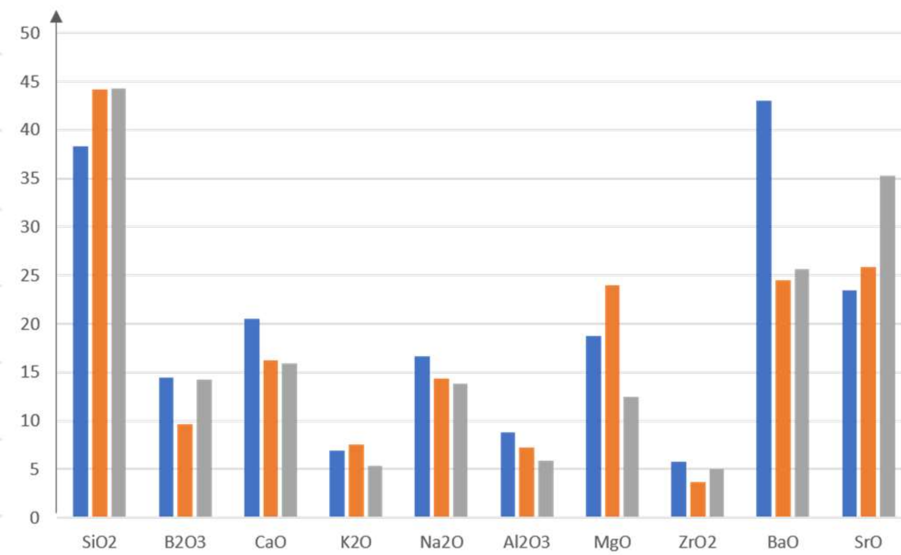
Seal type	Advantages	Disadvantages
Compressive seal	Easy replacement of seals in a manufacturing cell stack Resistance to thermal cycling	Application of external load Complex design and high cost **High gas leakage rate** Unsuitable for mobile applications **Poor stability** Electrically conductive
Viscous 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**

Evolution from 2020 to 2022

Constituents evolution in glass seal



Composition evolution in glass seal



2020 **2021** **2022**

Functions of different oxide in a seal glass

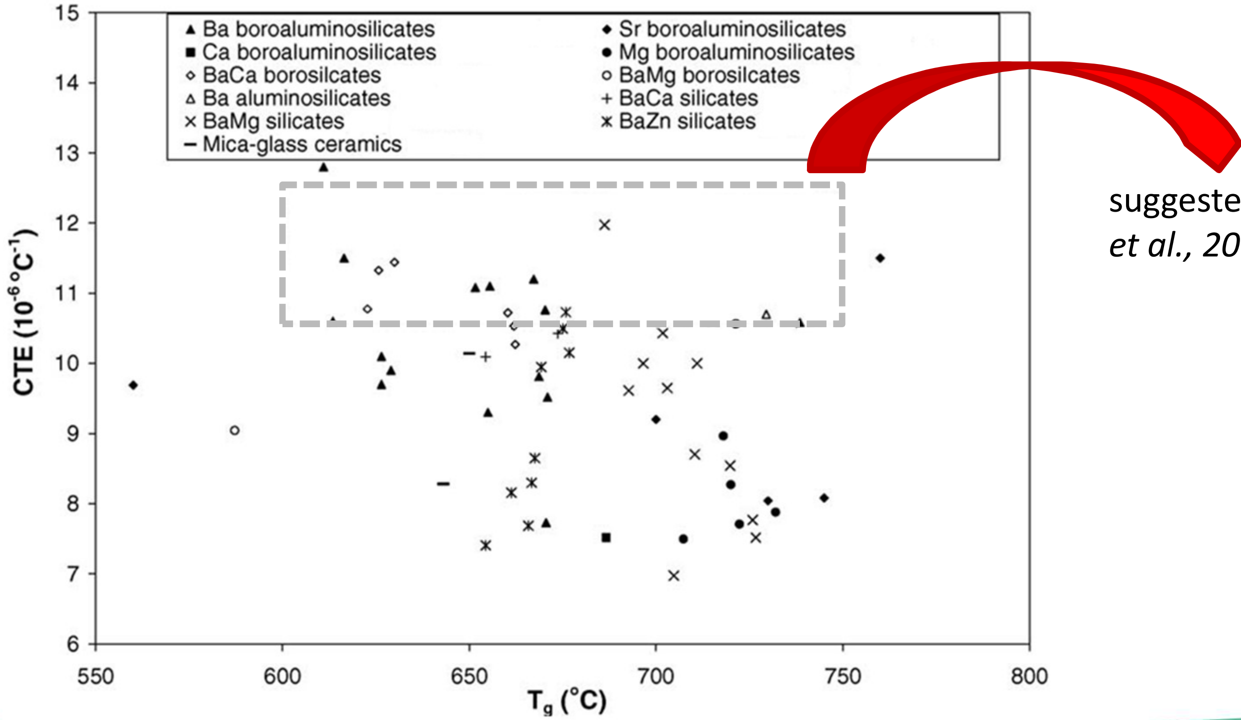
Glass constituent	Oxide	Function
Network former	SiO_2, B_2O_3	Form glass network Determine T_g and T_s Determine thermal expansion coefficient Determine adhesion/wetting with other SOFC/SOEC components
Network modifier	Li_2O, Na_2O, K_2O BaO, SrO, CaO, MgO	Maintain charge neutrality Create non-bridging 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

Sealants for SOFC/SOEC

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

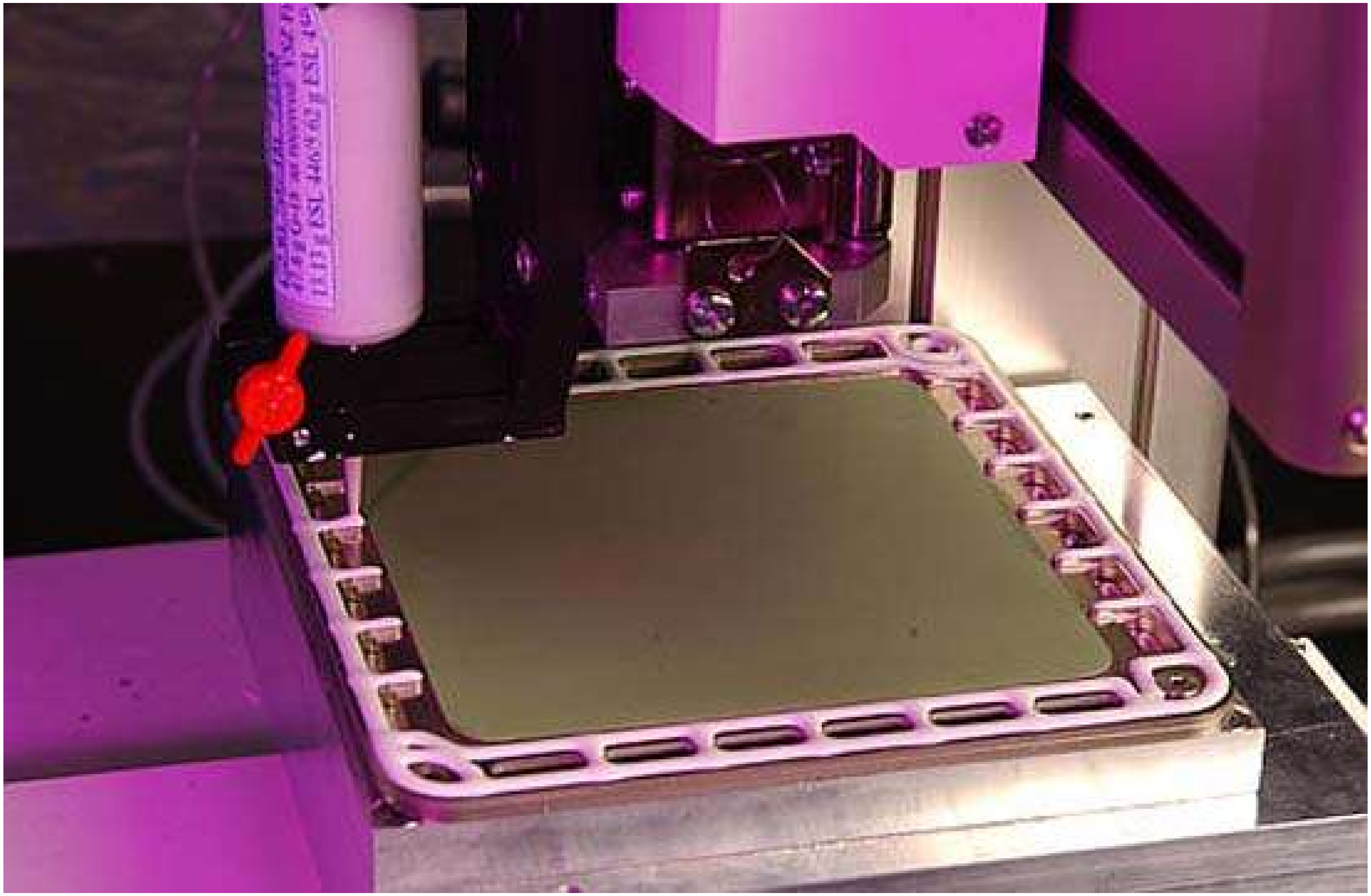
⇒ **glass transition temperature, T_g** (because of the glass must flow sufficiently to provide an adequate seal, while maintaining sufficient rigidity for mechanical integrity)

⇒ **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)

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

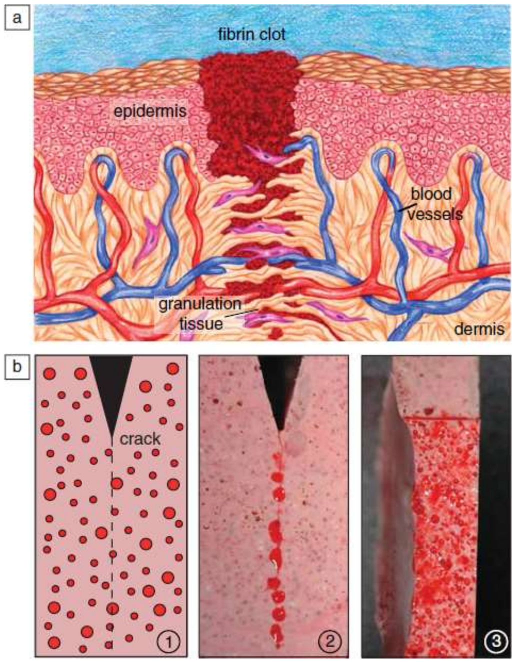
Design/System specific degradation

- 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)**

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

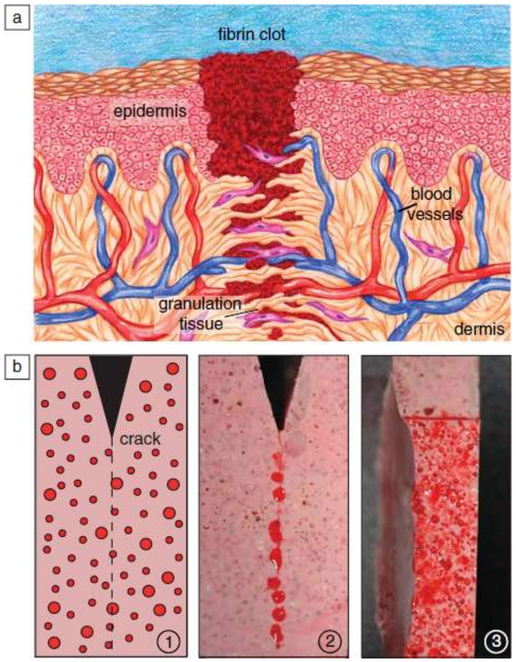
Self-healing: background



(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



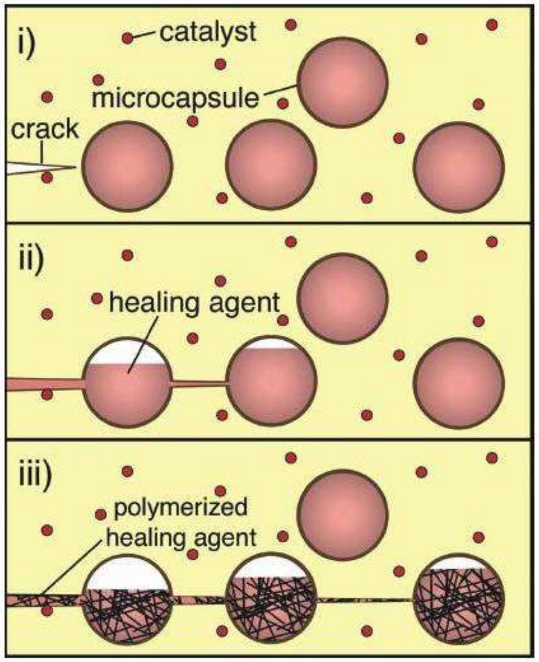
From J.P. Youngblood, MRS Bull. 2008

(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

(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

Self-healing material: 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: *glass sealant*

Increasing temperature in air

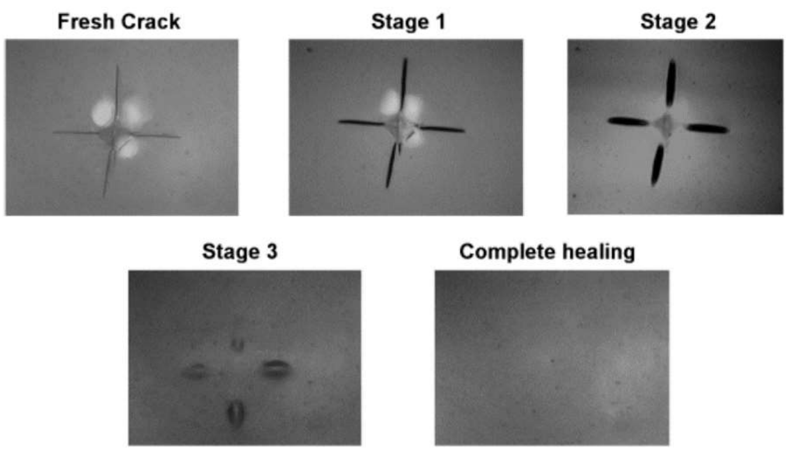
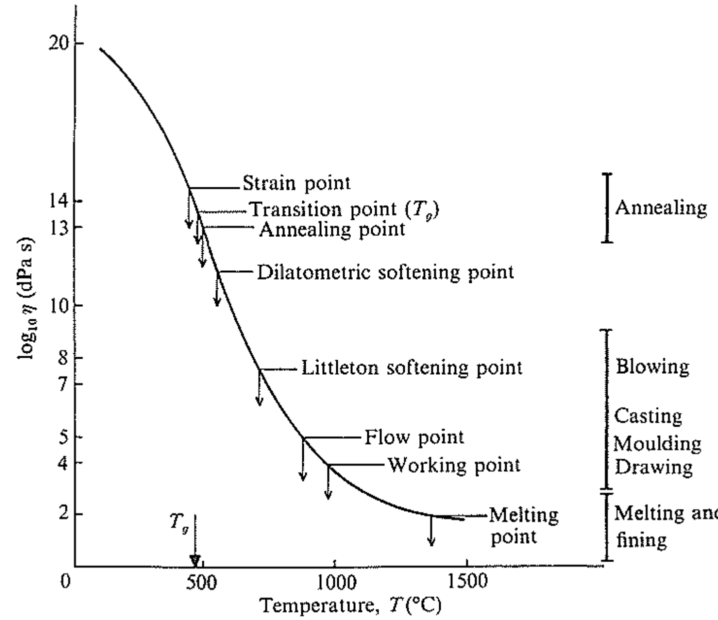


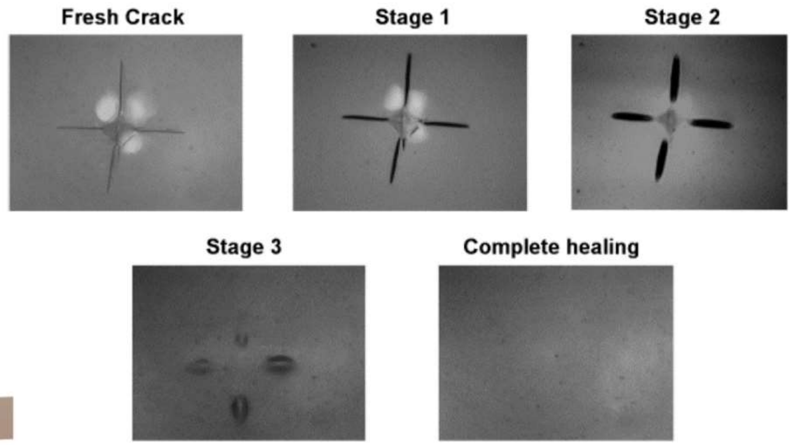
Fig. 4. Self-healing behavior of glass B indicating several stages of self-healing of cracks introduced by the microindentation technique (× 400) magnification.

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



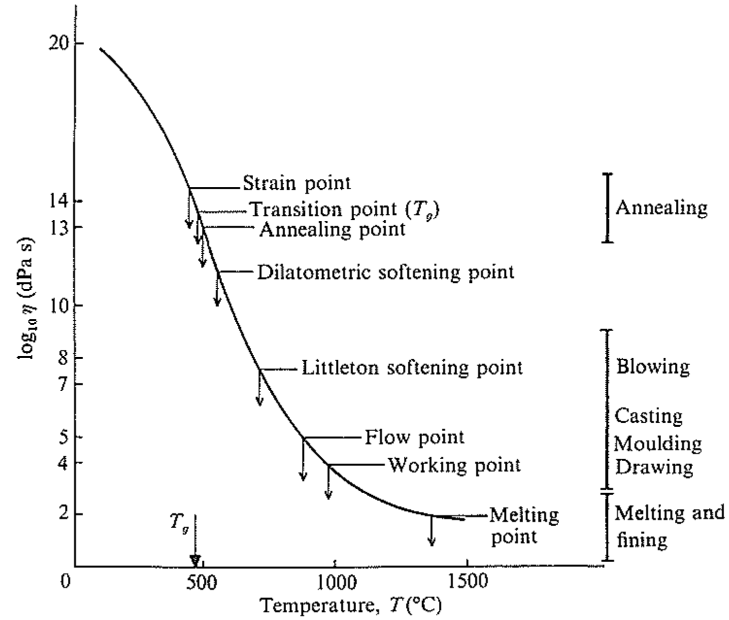
Non-autonomous self-healing: *glass sealant*

Increasing temperature in air



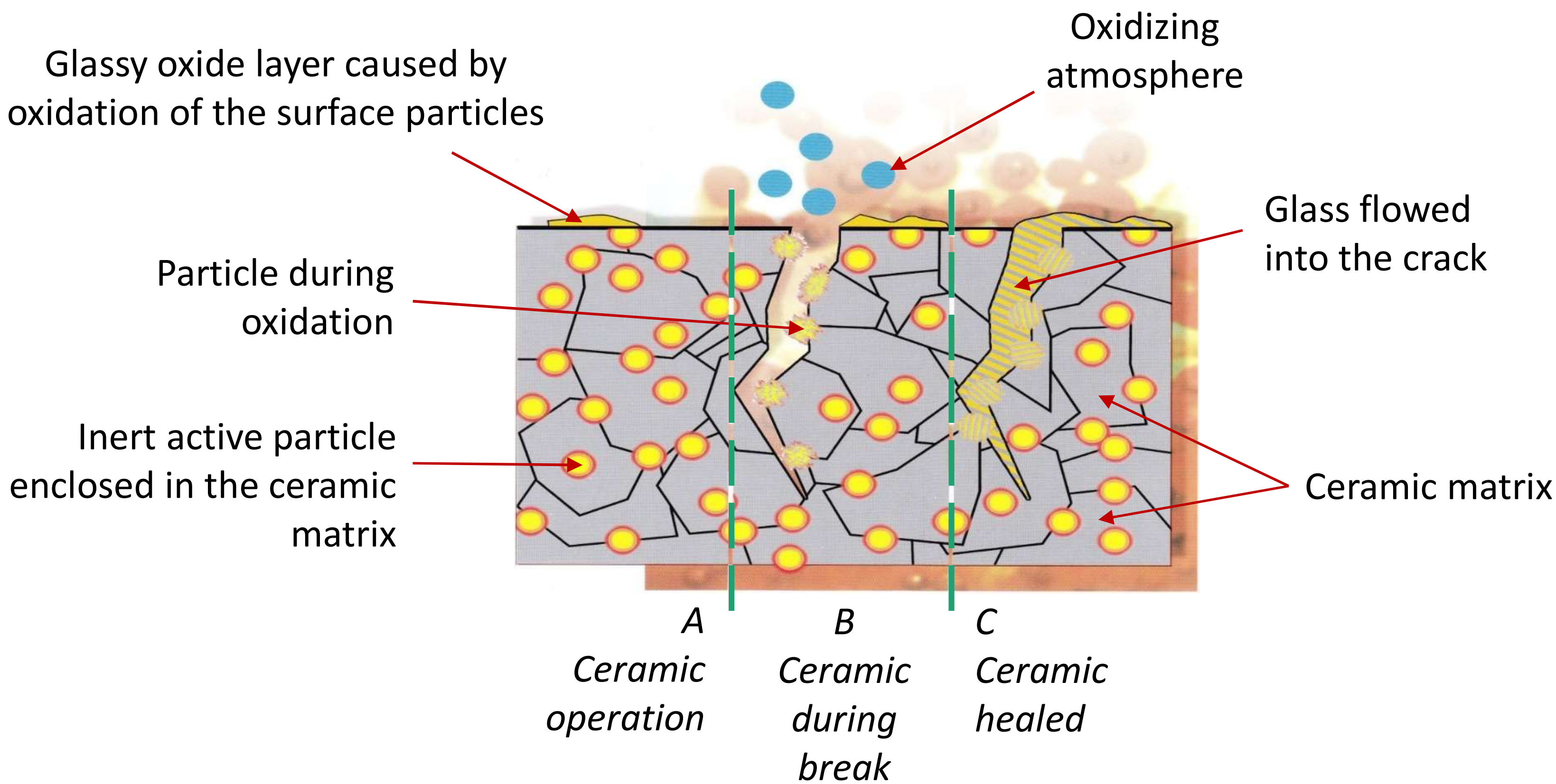
4. *Self-healing behavior of glass B indicating several stages of self-healing of cracks introduced by the microindentation technique × 400) magnification.*

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



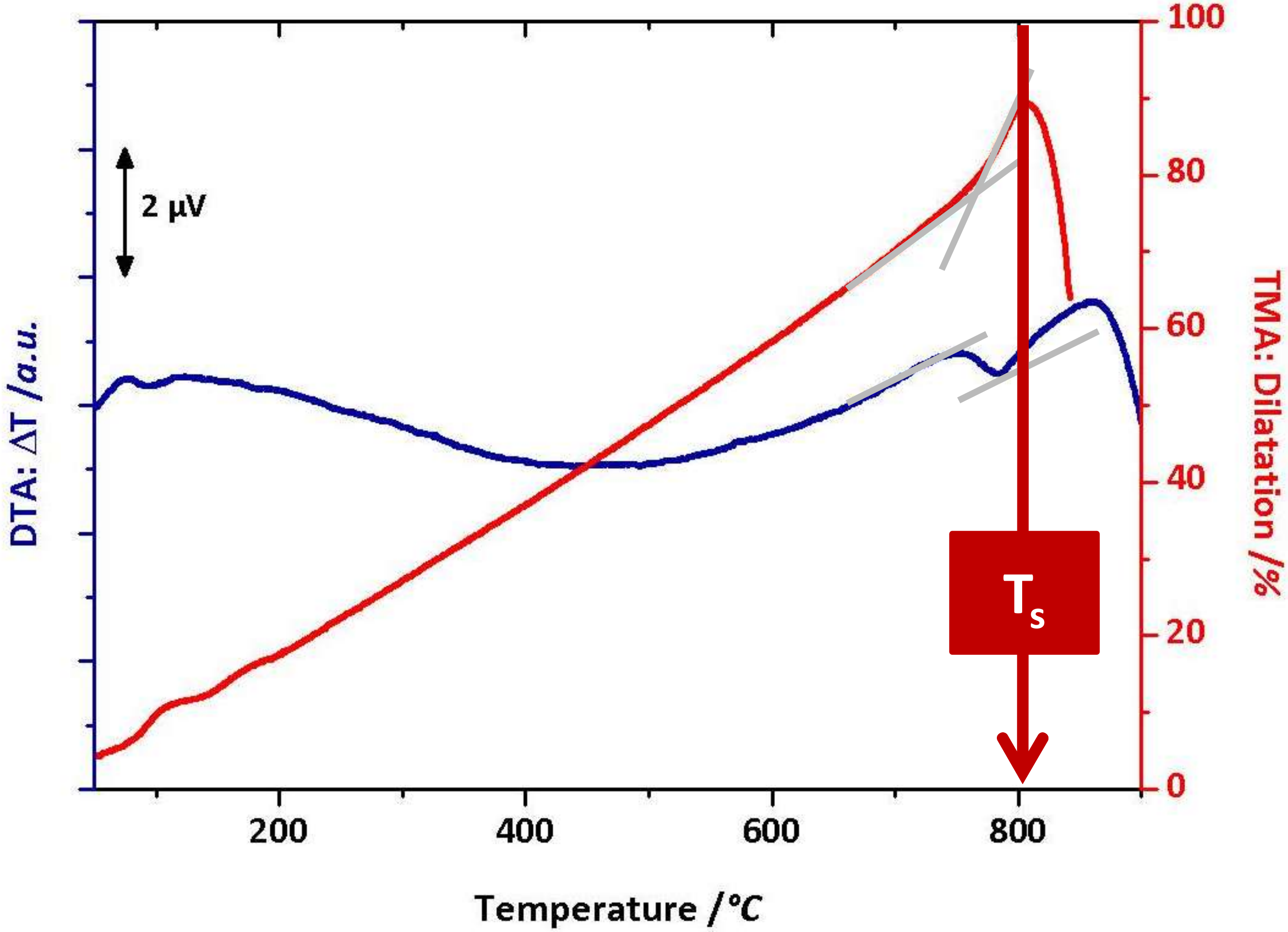
disappearance of damage due to the flow of the glass phase after heating at high operating temperature

Autonomous self-healing: *ceramic composite*

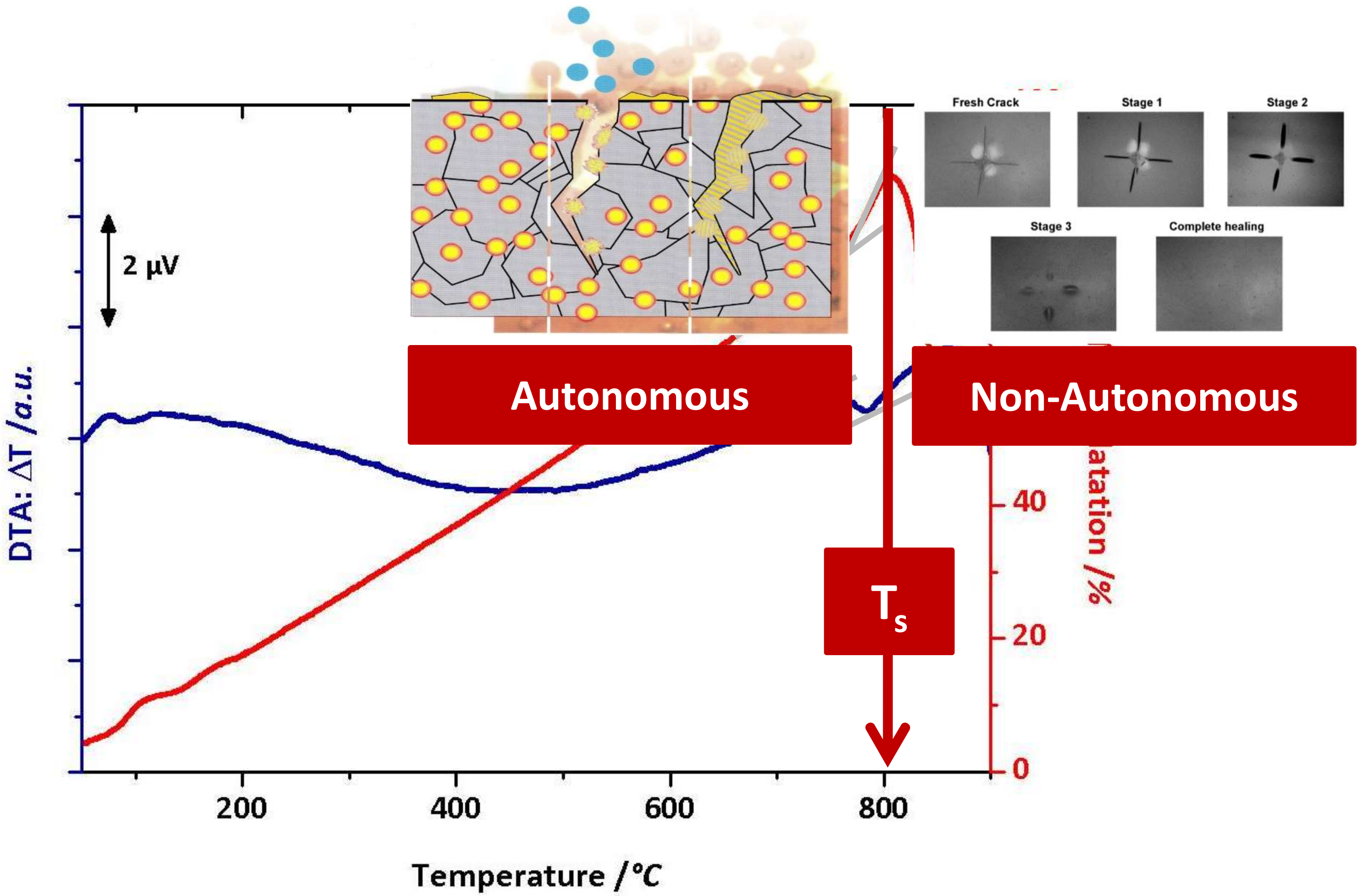


From S.K. Ghosh, Self Healing Materials: Fundamentals, Design Strategies and Applications, Willey-VCH 2009

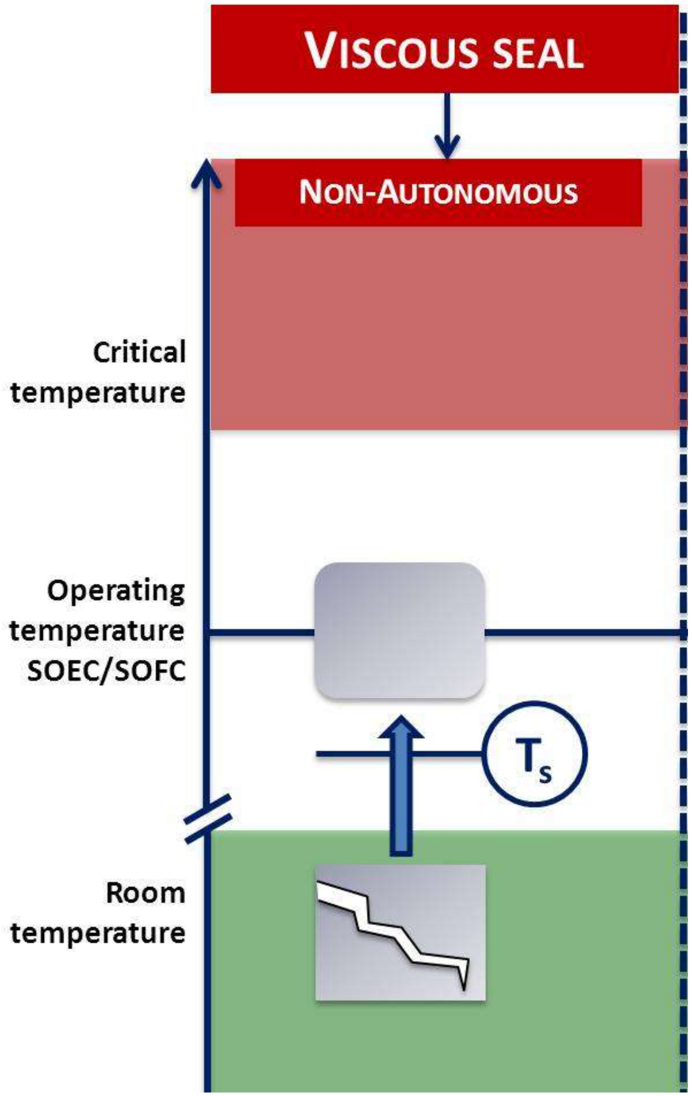
Self-healing glassy materials: *concept*



Self-healing glassy materials: *concept*



Self-healing glassy materials: *concept*



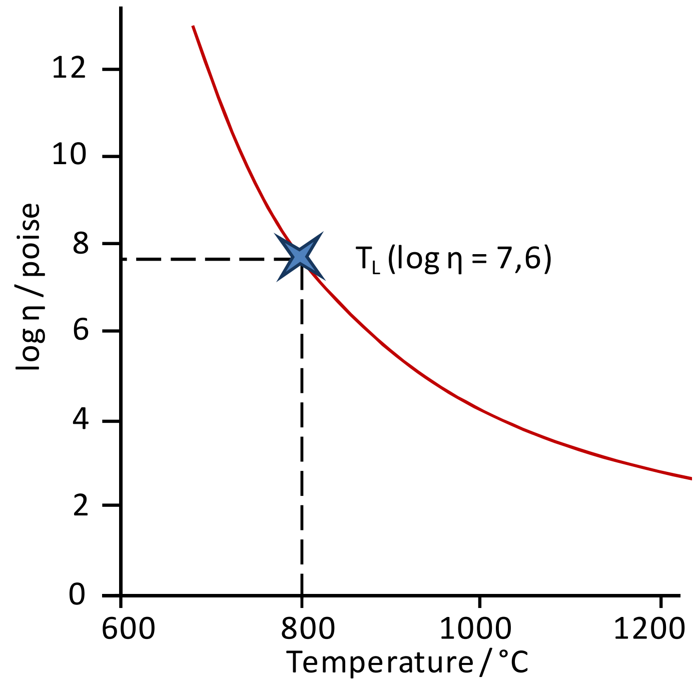
Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ 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)

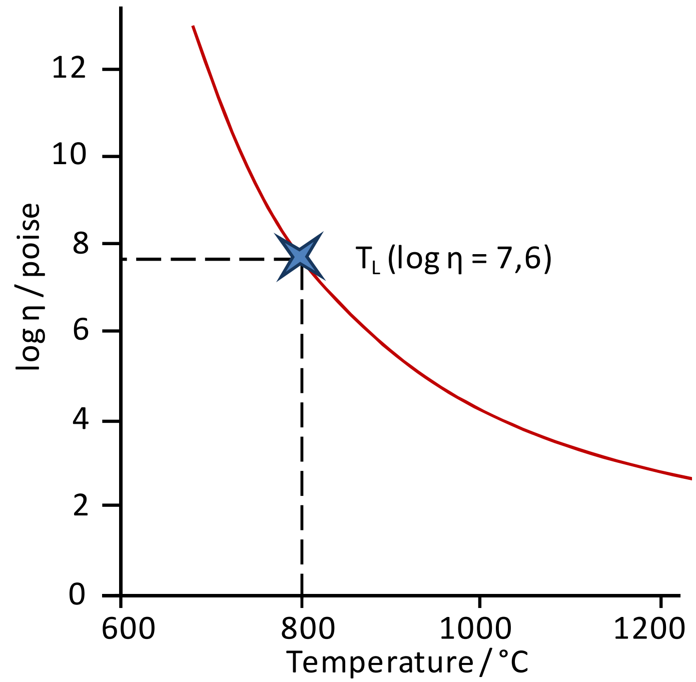
→ $T_g > 600$˚C
→ 750˚C < $T_{Littleton}$ < 900˚C
→ TEC > 5×10^{-6} K^{-1}
→ Limited amount of P_2O_5



Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ 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}
→ Limited amount of P_2O_5

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

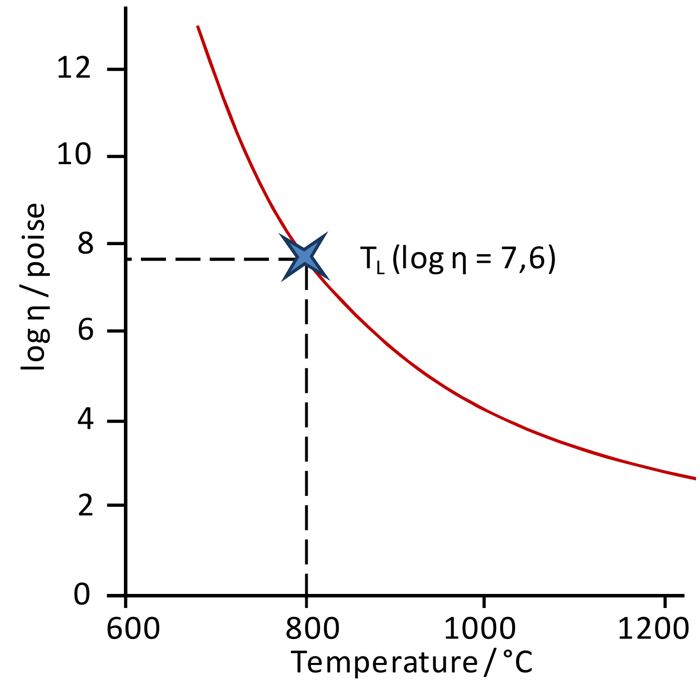
Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ 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}
→ Limited amount of P_2O_5

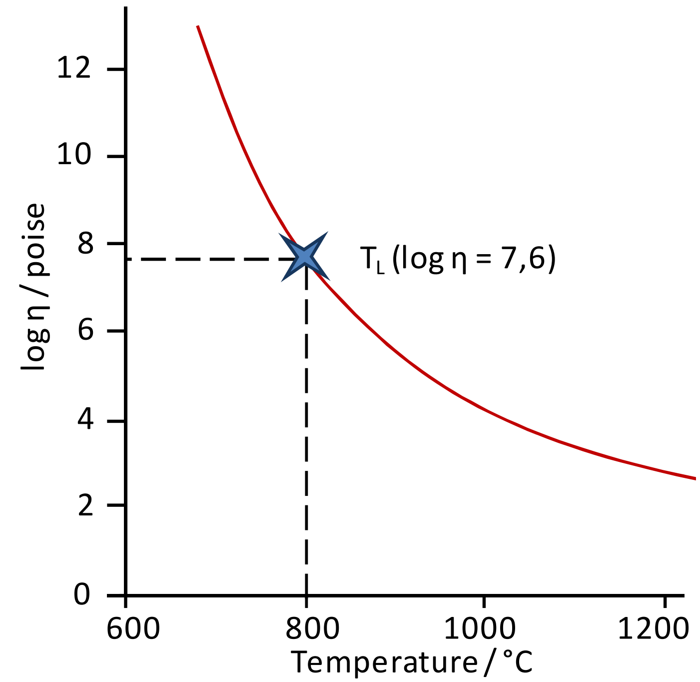


Molar %	SiO_2	ZrO_2	B_2O_3	Al_2O_3	Ga_2O_3	La_2O_3	Y_2O_3	Na_2O	K_2O	CaO	BaO	ZnO	MgO	SrO	Crystallisation	T_g / °C
Vsc1	70.24	-	1.92	5.26	-	-	-	3.60	1.19	0.60	3.32	9.05	4.82	-	Yes	650
Vsc2	63.30	-	-	-	-	-	4.99	20.72	6.81	4.45	-	-	-	-	Yes	566
Vsc3	67.46	13.34	-	-	-	1.03	-	13.67	4.50	-	-	-	-	-	No	765
Vsc4	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

Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ 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}
→ Limited amount of P_2O_5

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

Viscous seal for SOEC

Requirements

→ $T_{Littleton}$ ($\eta = 10^{7.6}$ Poise) = 800˚C
→ Low viscosity at 900˚C
→ No crystallization at 800˚C

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

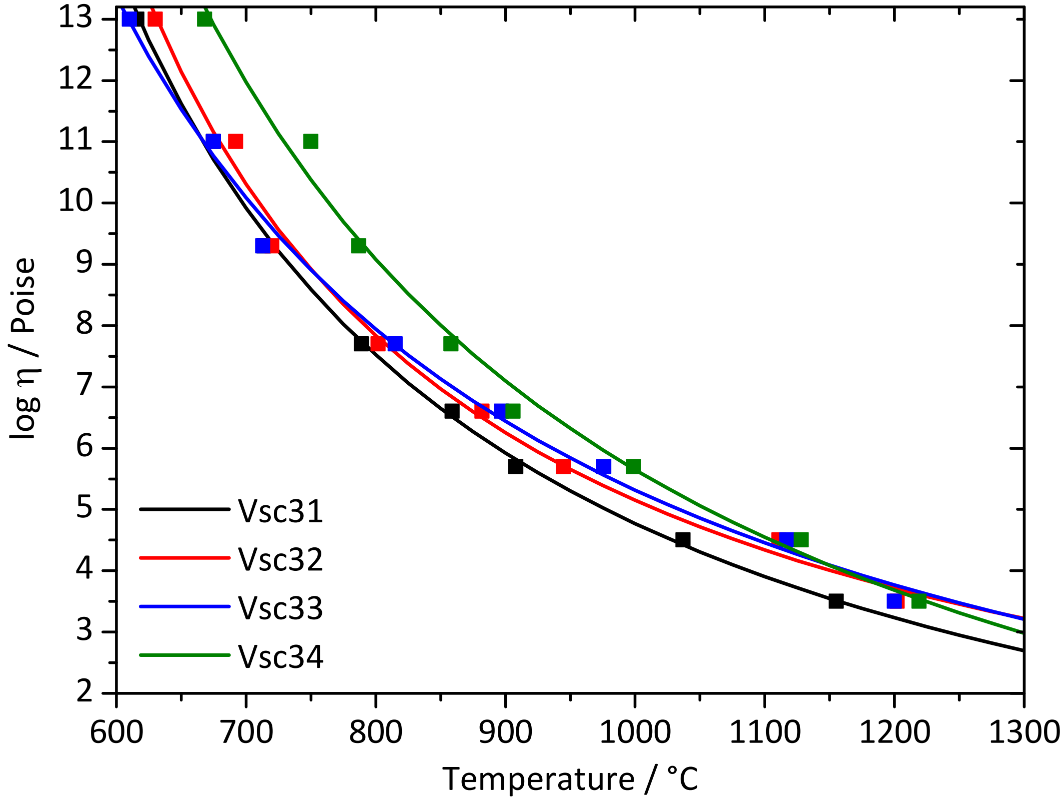
Viscous seal for SOEC

HSM Measurements

→ Applying the method to Vsc glasses

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

$$\text{Log}\,\eta = a + \frac{b}{T - t}$$

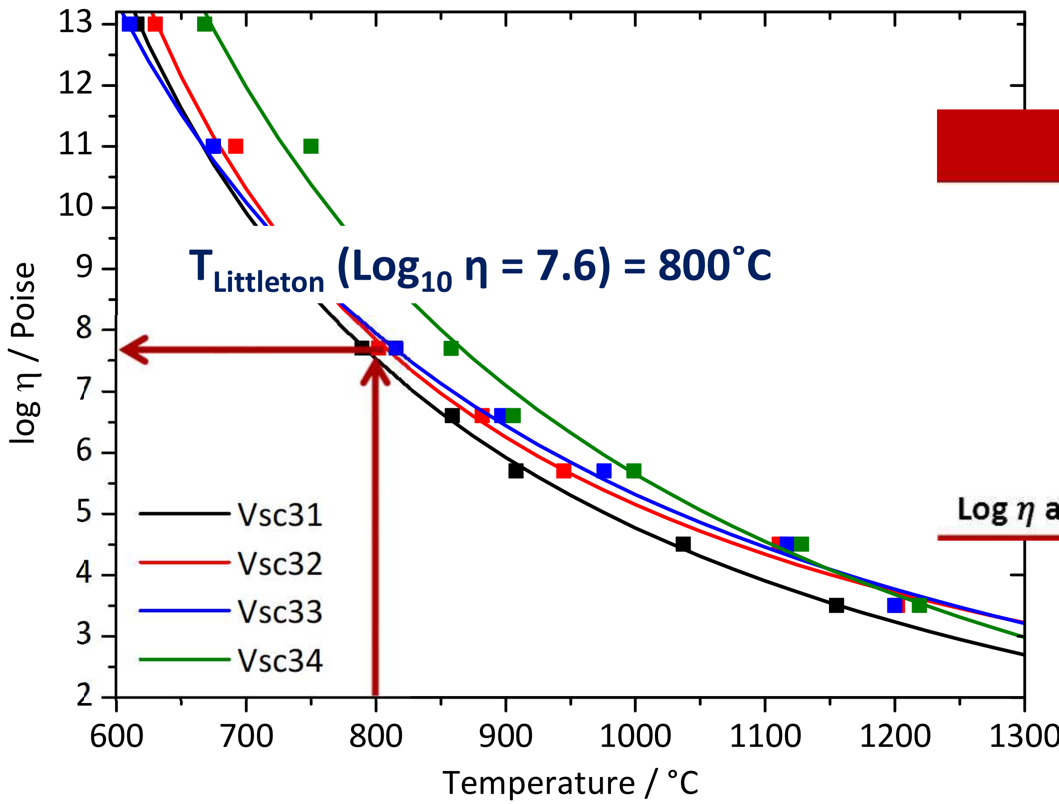


Viscous seal for SOEC

HSM Measurements

→ Applying the method to Vsc glasses

→ Least-square refinement by Vogel-Fulcher-Tammann equation: $\text{Log}\,\eta = a + \dfrac{b}{T - t}$



	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

[redacted]

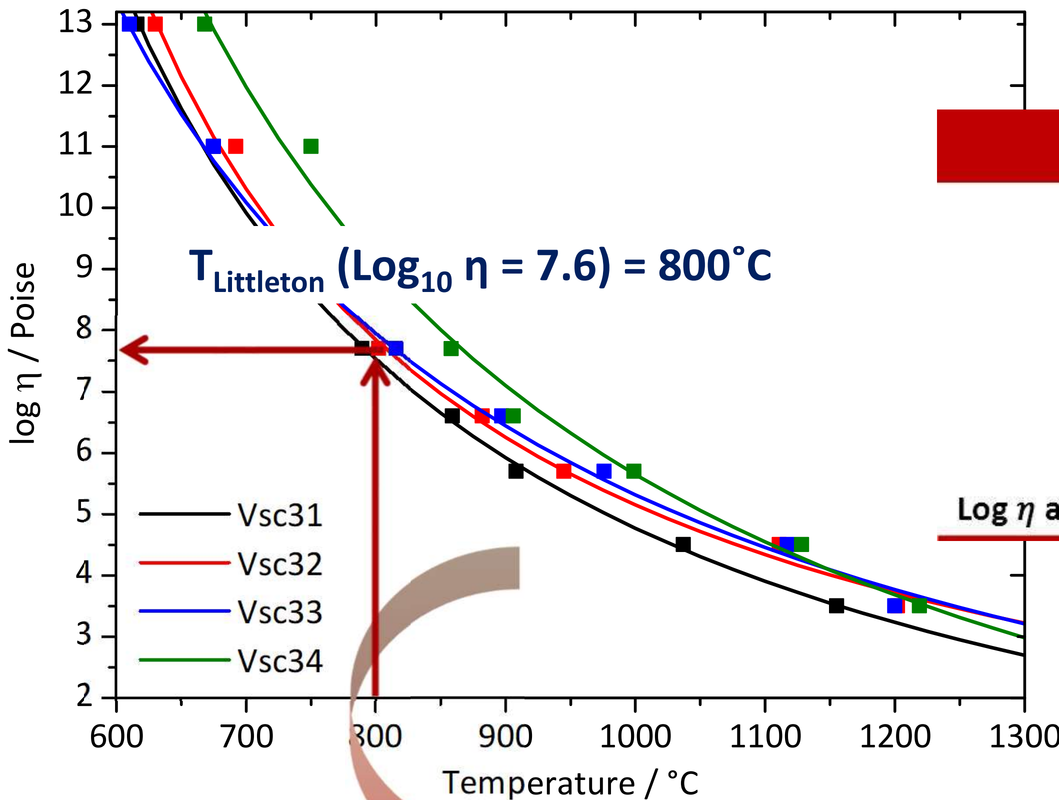
Viscous seal for SOEC

HSM Measurements

→ Applying the method to Vsc glasses

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

$$\text{Log}\,\eta = a + \frac{b}{T - t}$$



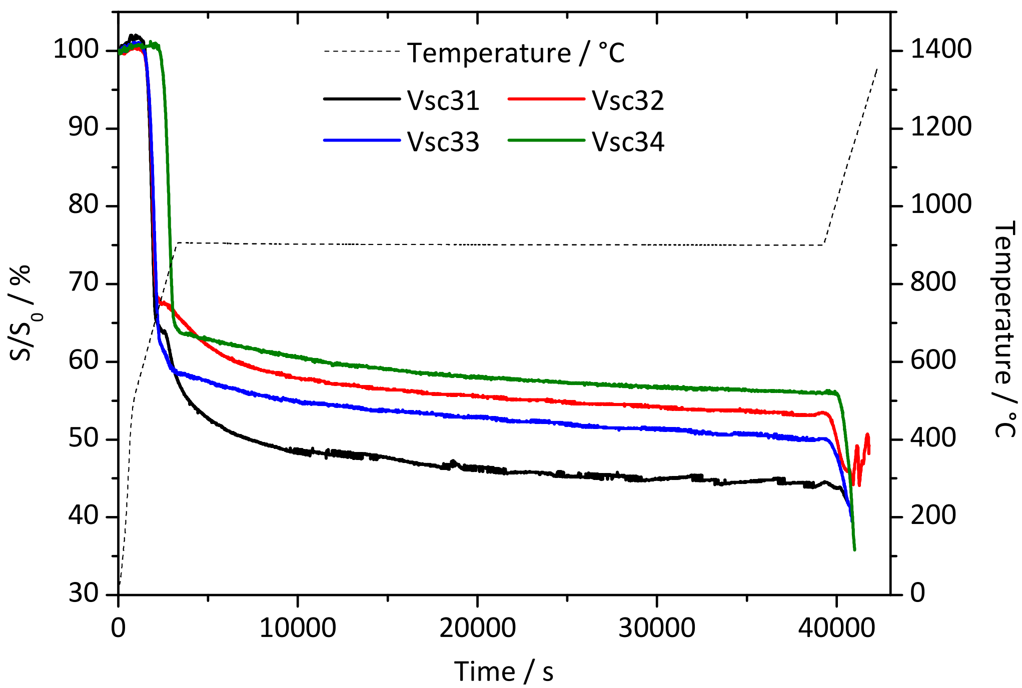
	Vsc31	Vsc32	Vsc33	Vsc34
a	-2.19	-1.00	-2.24	-3.58
b	4917.52	4053.35	5863.19	6809.79
t	293.96	341.80	224.28	262.17
T_L / °C	796	813	820	871
Log η at 900°C / Poise	5.9	6.3	6.4	7.1

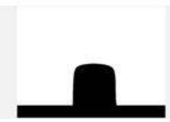
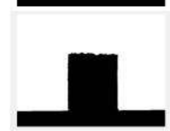
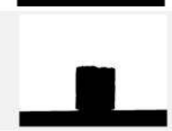
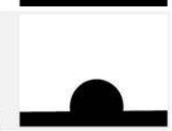
Only Vsc31, Vsc32 and Vsc33 appear suitable

Viscous seal for SOEC

HSM Measurements

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

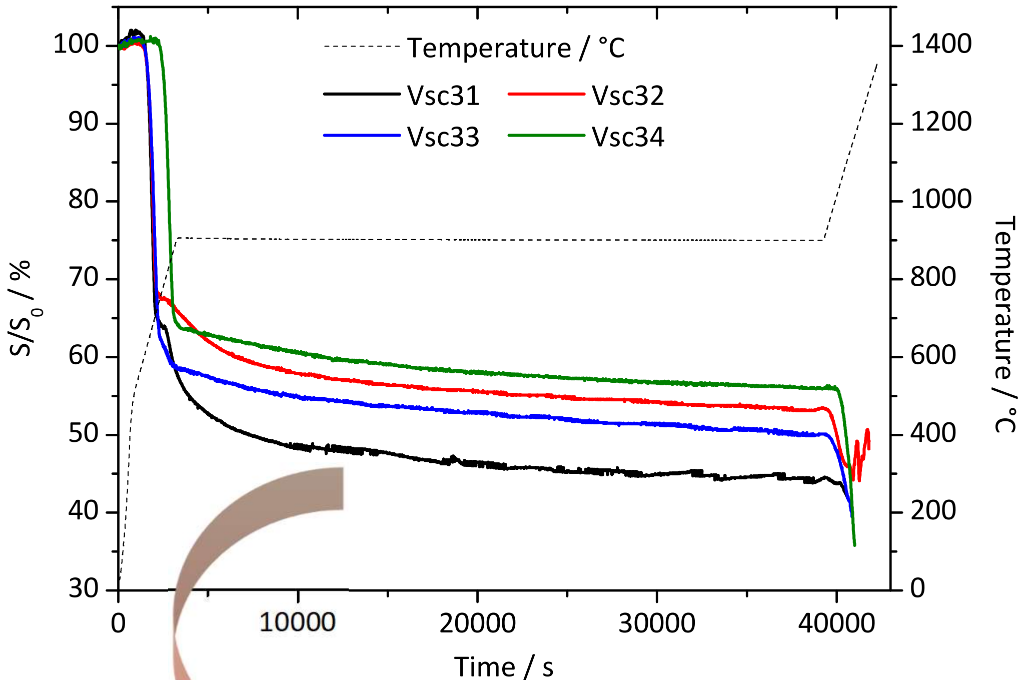


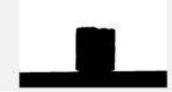
Glass name and viscosity at 900°C	Initial pellet	Pellet before the plateau at 900°C	Pellet after the plateau
Vsc31 $10^{5.9}$ Poise			
Vsc32 $10^{6.3}$ Poise			
Vsc33 $10^{6.4}$ Poise			
Vsc34 $10^{7.1}$ Poise			

Viscous seal for SOEC

HSM Measurements

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



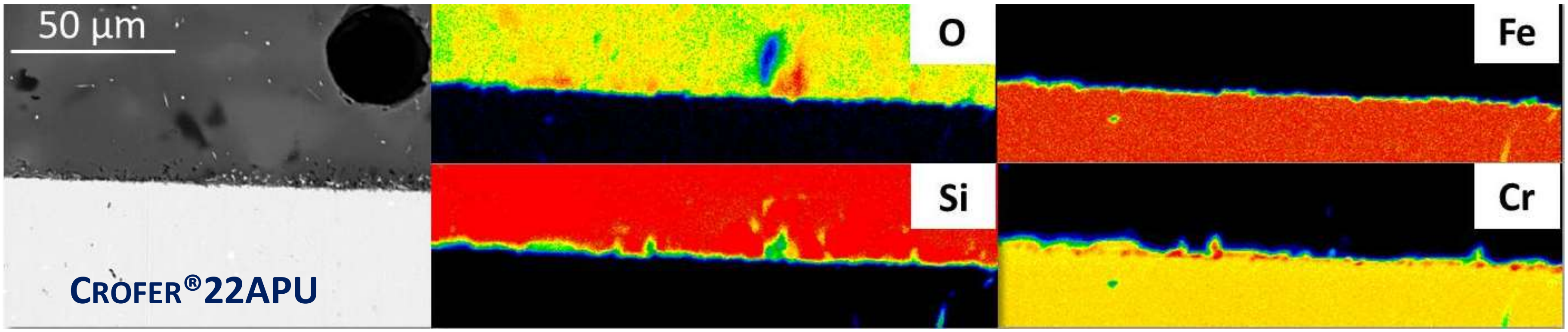
Glass name and viscosity at 900°C	Initial pellet	Pellet before the plateau at 900°C	Pellet after the plateau
Vsc31 $10^{5.9}$ Poise			
Vsc32 $10^{6.3}$ Poise			
Vsc33 $10^{6.4}$ Poise			
Vsc34 $10^{7.1}$ Poise			

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

Viscous seal for SOEC: *stability*

Castaing Microprobe Observations

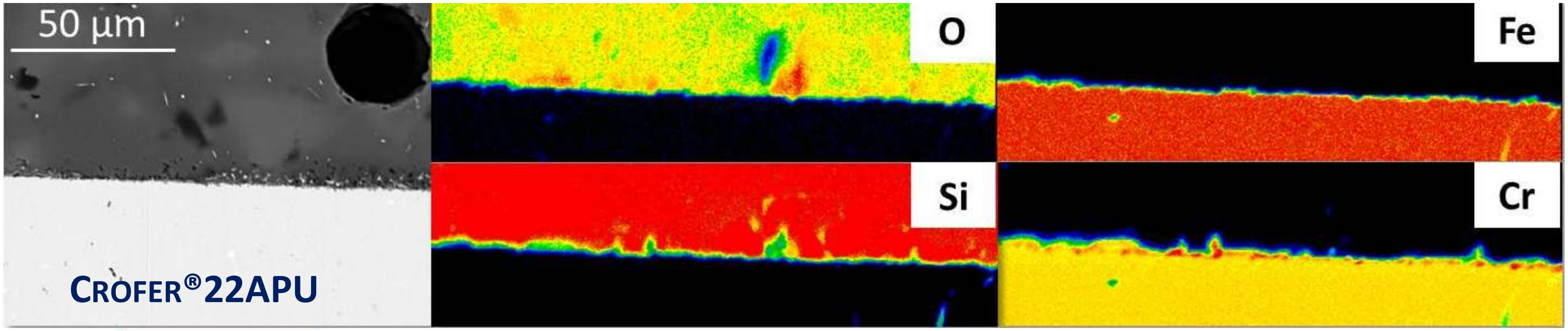
Vsc31 ⇒ chromium oxide formation at the interface (1.4 µm)



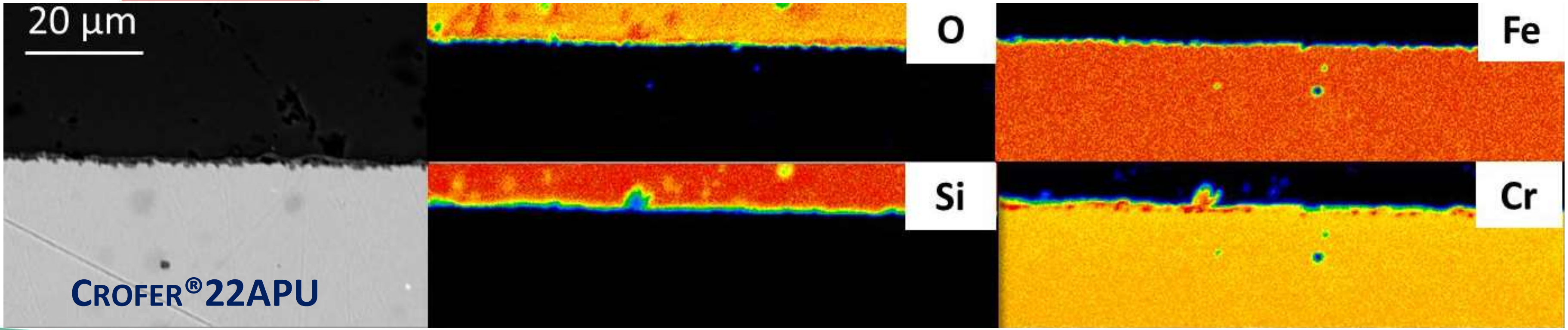
Viscous seal for SOEC: *stability*

Castaing Microprobe Observations

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



Vsc32 ⇒ chromium oxide formation at the interface (1.8 µm)

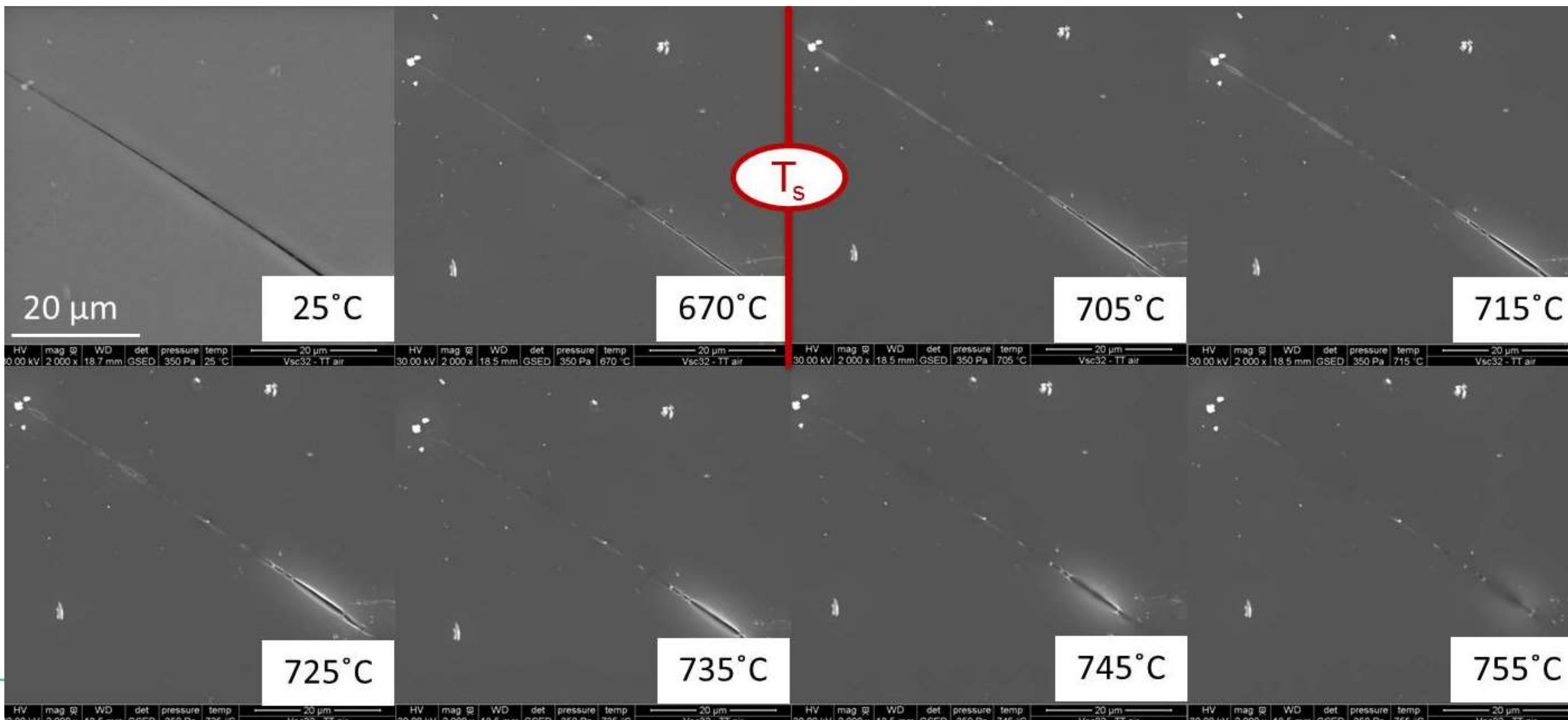


In situ observation of crack healing

In situ **Observations by HT-ESEM**

Vsc32 / Air

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

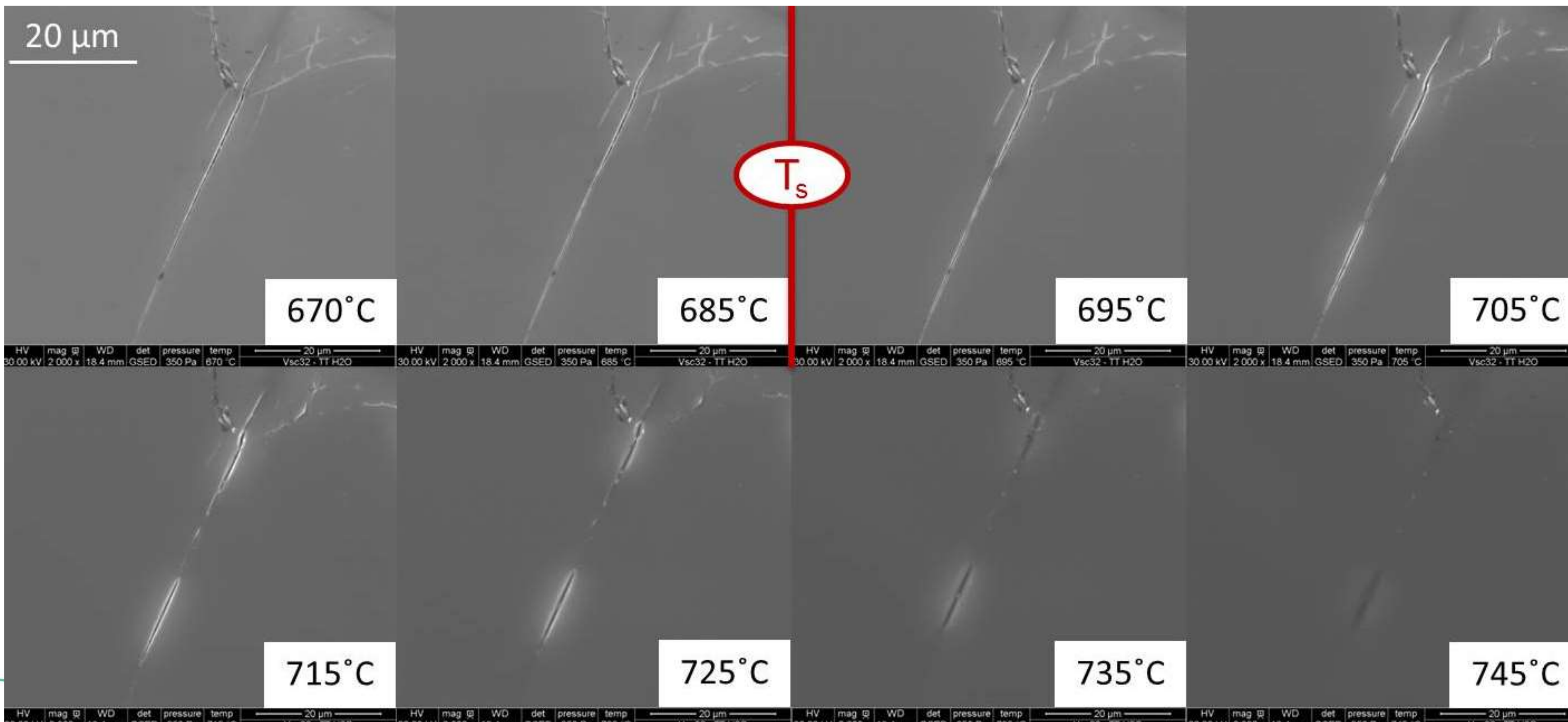


In situ observation of crack healing

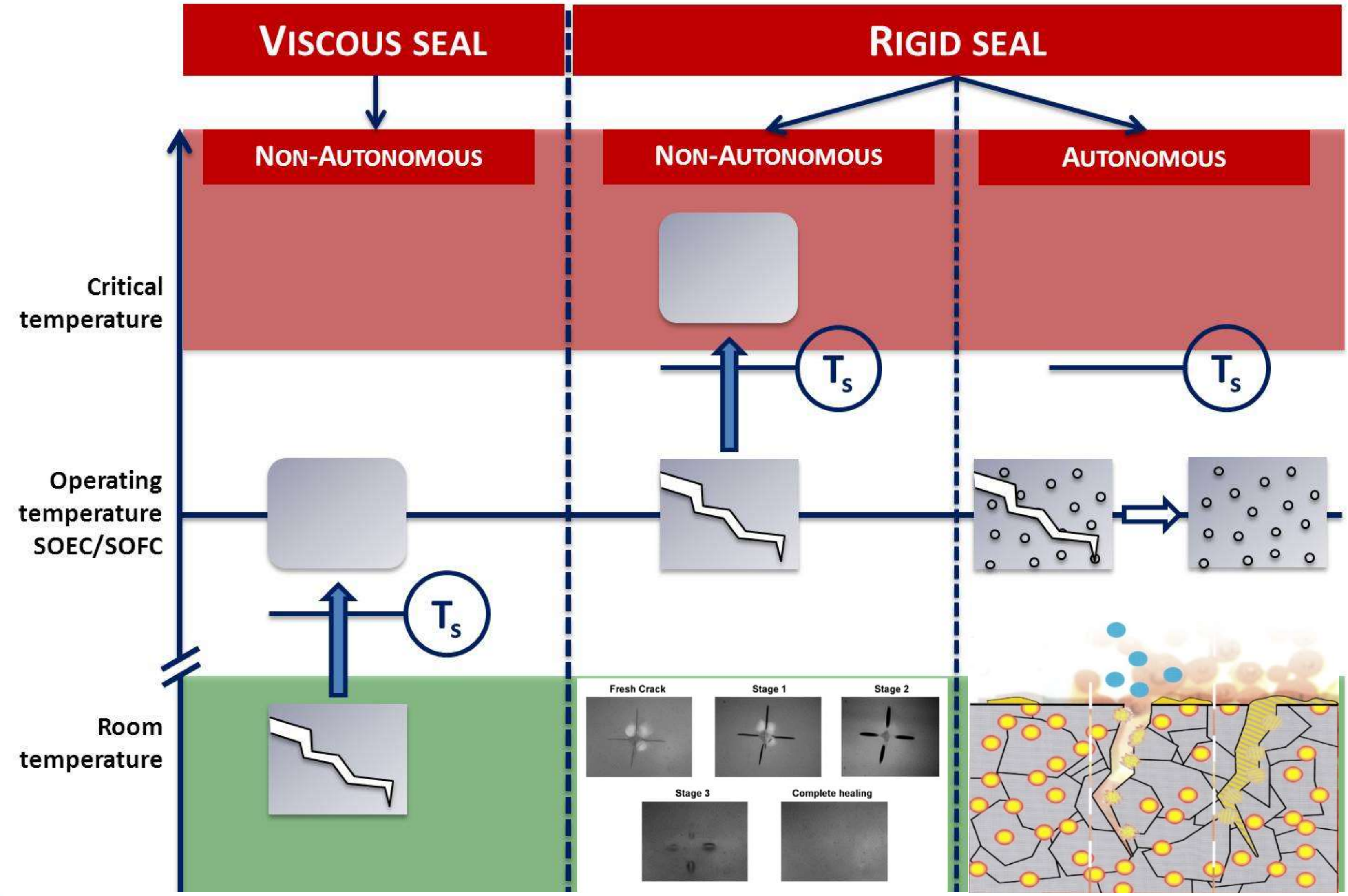
***In situ* Observations by HT-ESEM**

Vsc32 / H_2O

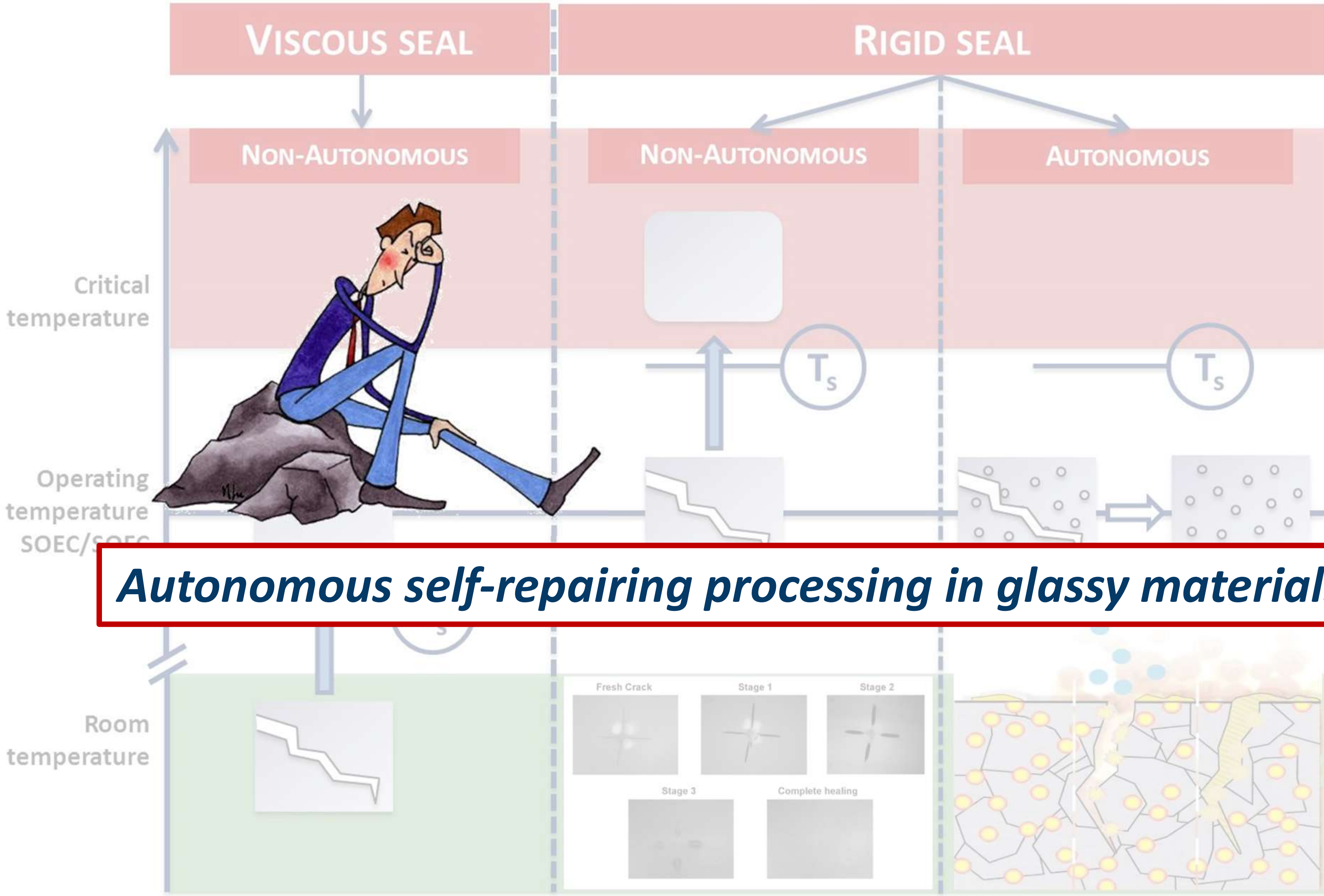
	Start of healing	End of healing
Temperature / °C	670	745
Viscosity / Poise	11.38	9.27



Self-healing glassy materials: *concept*



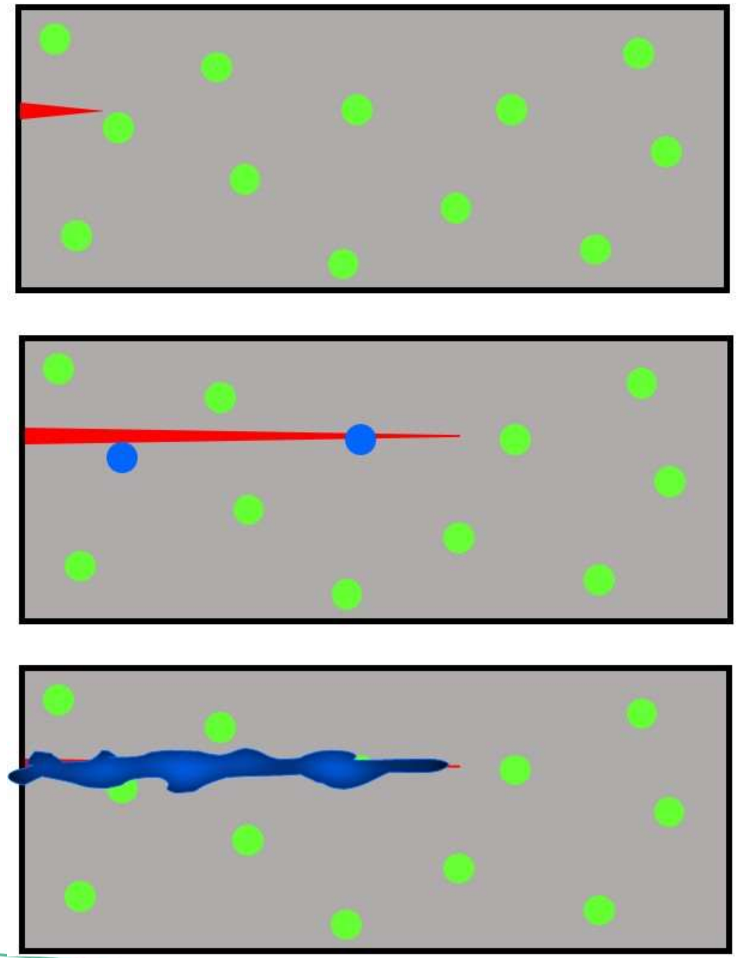
Self-healing glassy materials: *concept*



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**

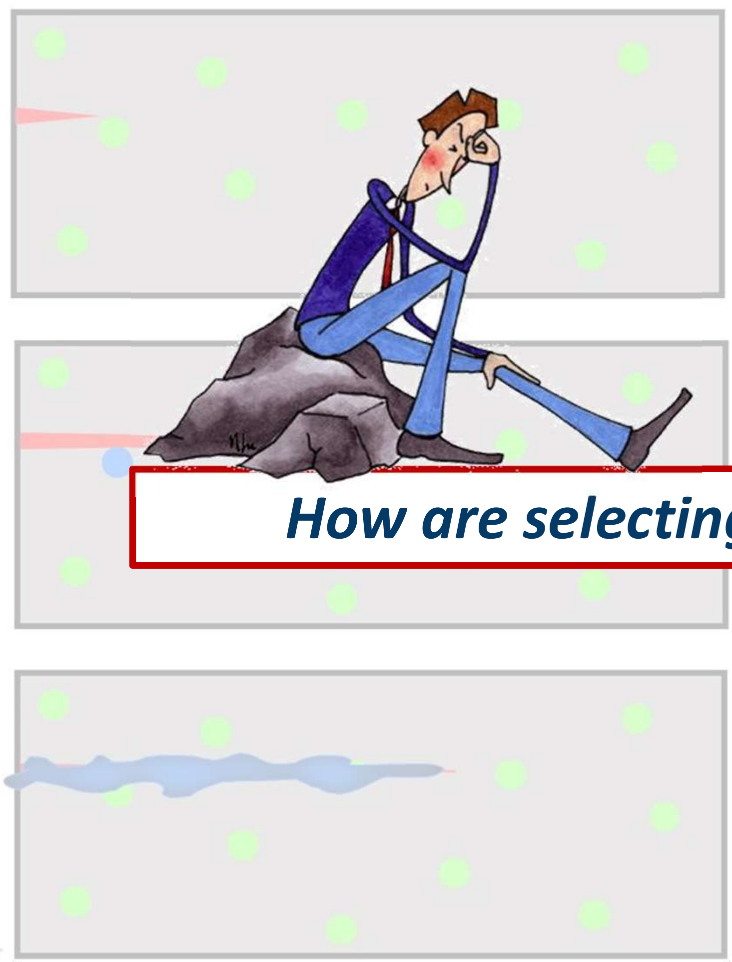
→ **Contact of O_2 contained into atmosphere with some active particles leading to their oxidation**

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

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

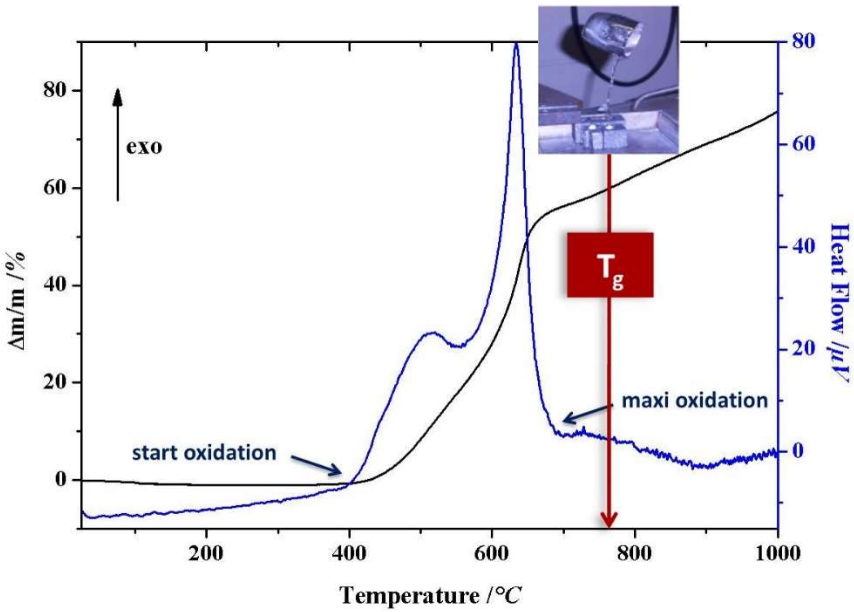
How are selecting the healing particles ?

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

Patent WO 2010/136721 A1

Healing agent selectivity: *VB*

Differential thermal analysis



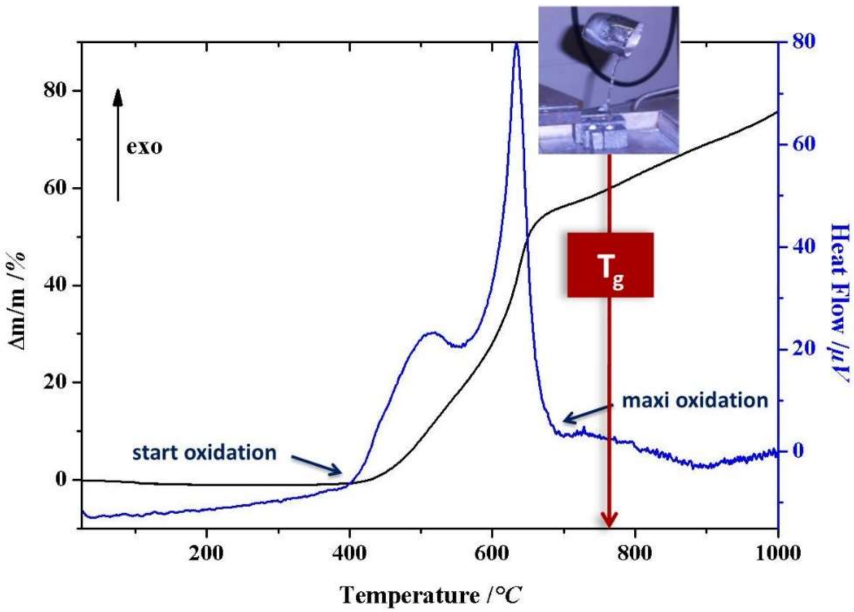
→ stable at working temperature in the absence of air

→ oxidize rapidly in the presence of air

→ oxides must be fluid at the working temperature

Healing agent selectivity: *VB*

Differential thermal analysis

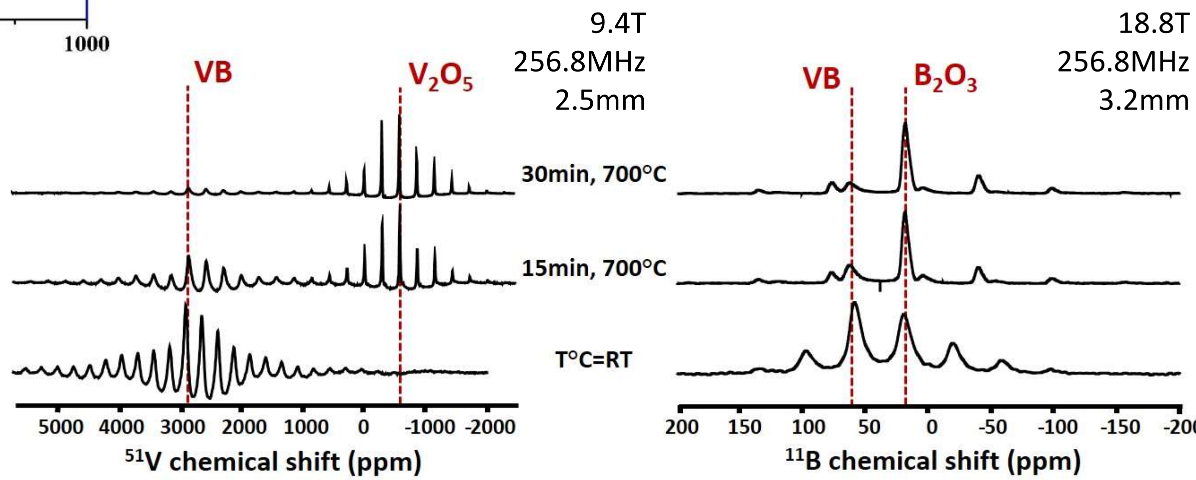


→ stable at working temperature in the absence of air

→ oxidize rapidly in the presence of air

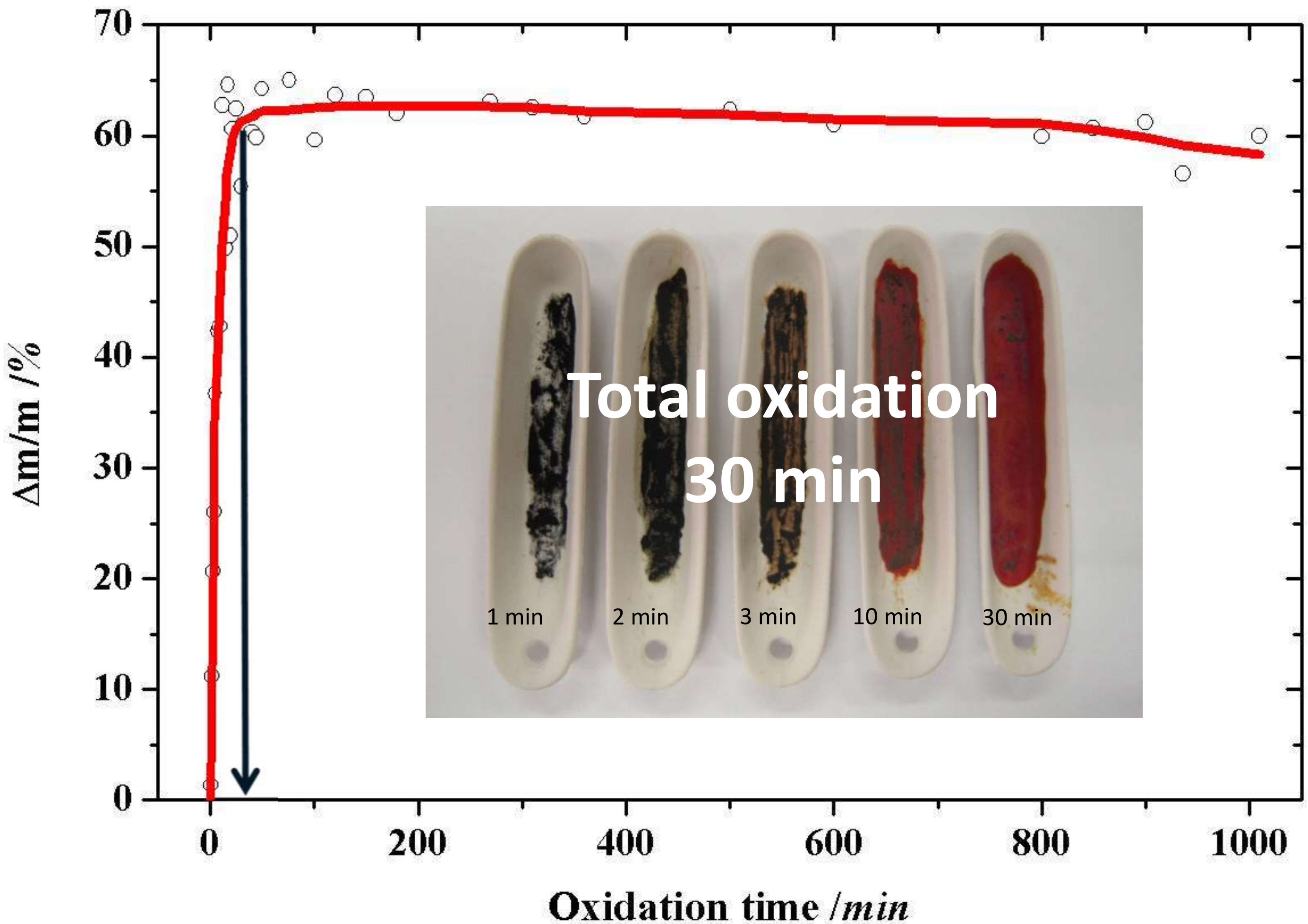
→ oxides must be fluid at the working temperature

Nuclear magnetic resonance



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

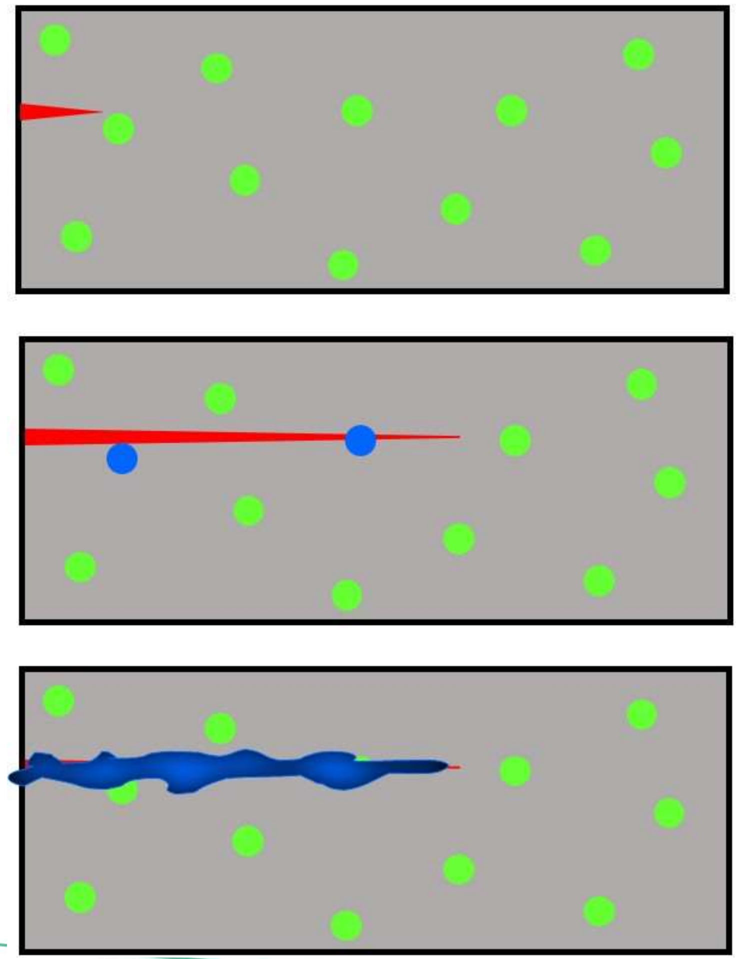
Healing agent selectivity: *VB*

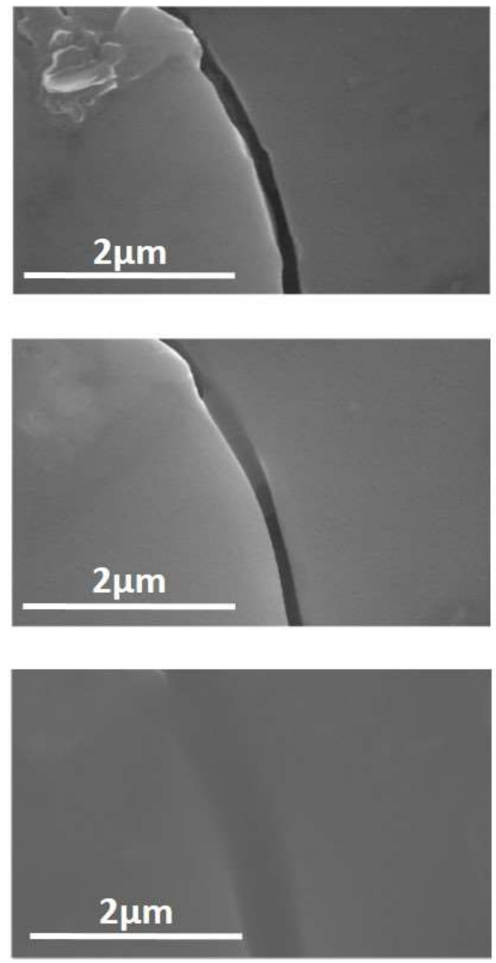


In situ observation of crack healing

Autonomous self-healing glass matrix upon occurrence of cracks

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

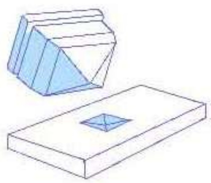




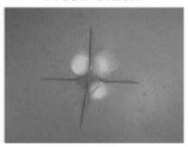
In situ observation of crack healing

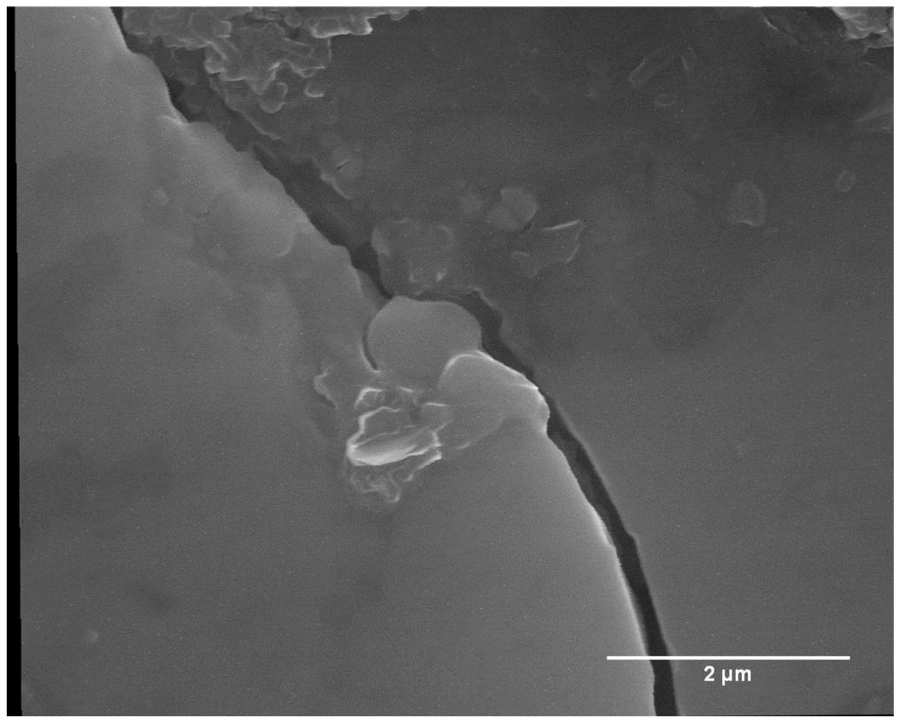
Environmental microscopy (HT-ESEM)

<u>Conditions</u>: 700˚C, P_{O2} = 450Pa



Fresh Crack



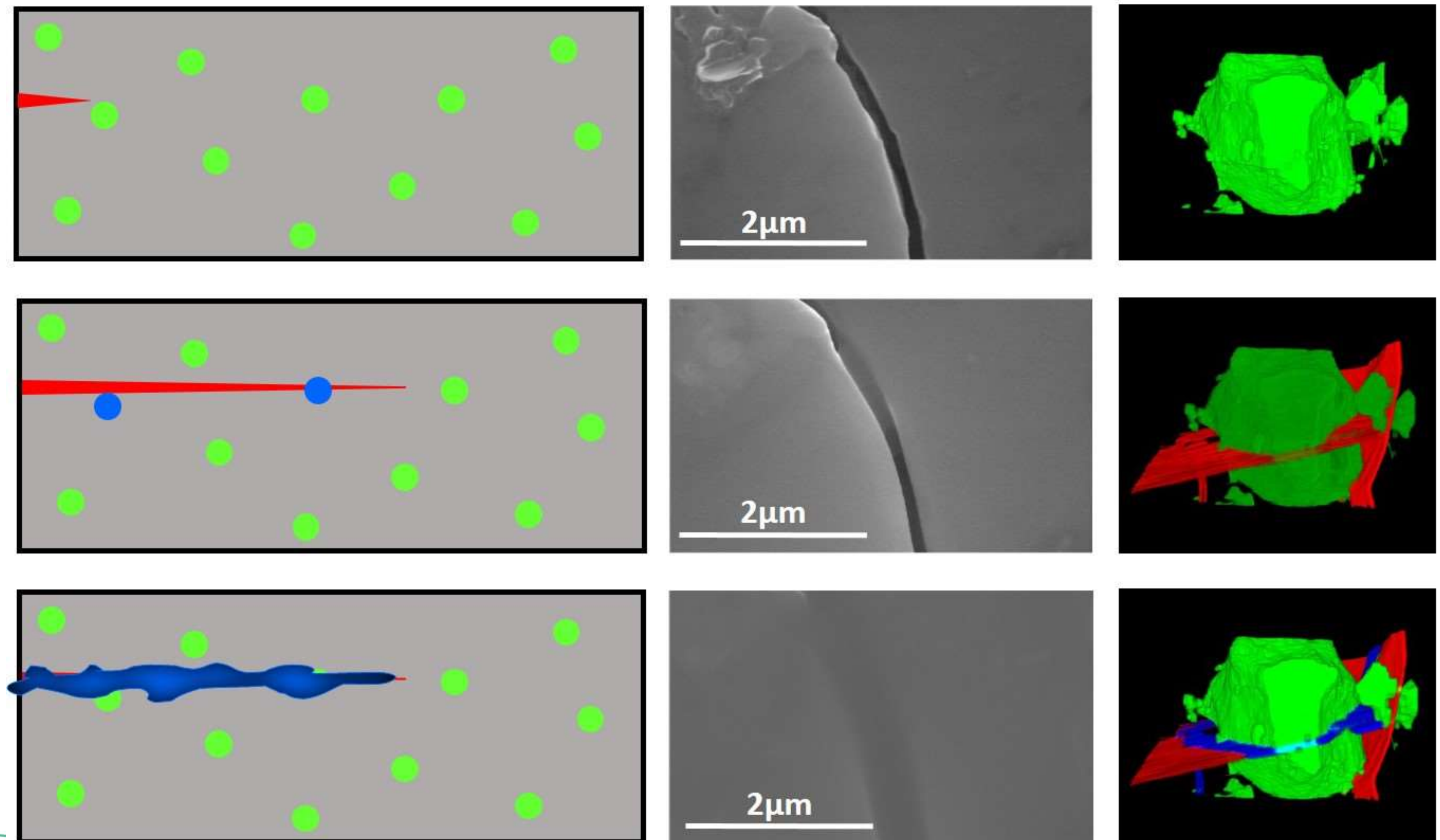


Isothermal treatment at 700˚C in air:

→ oxidation of VB particles and formation of V_2O_5 and B_2O_3

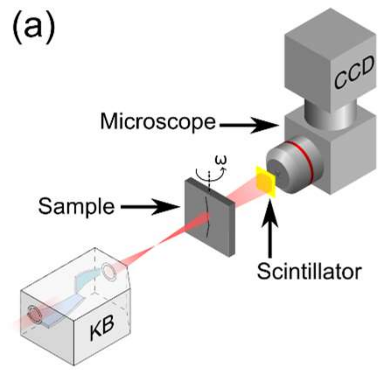
Ex situ observation of crack healing

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)

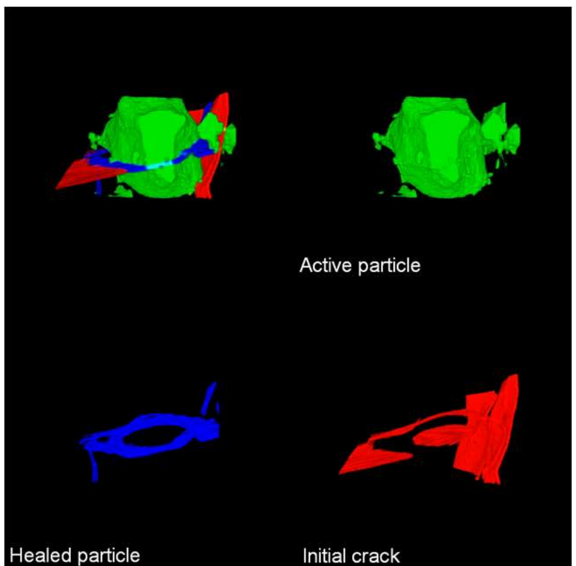


Ex situ observation of crack healing

X-ray nano-imaging (ID22NI)



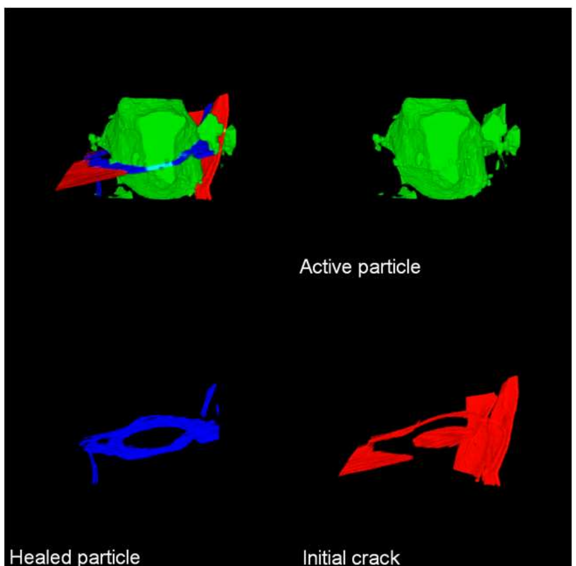
X-ray nano-tomography image reconstitution of a crack throughout the material

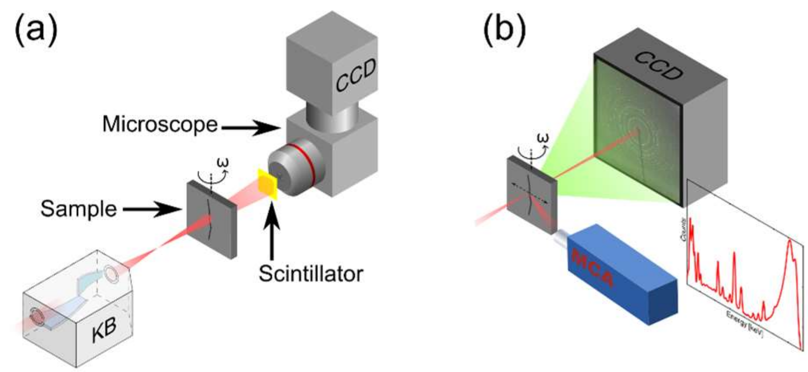


Ex situ observation of crack healing

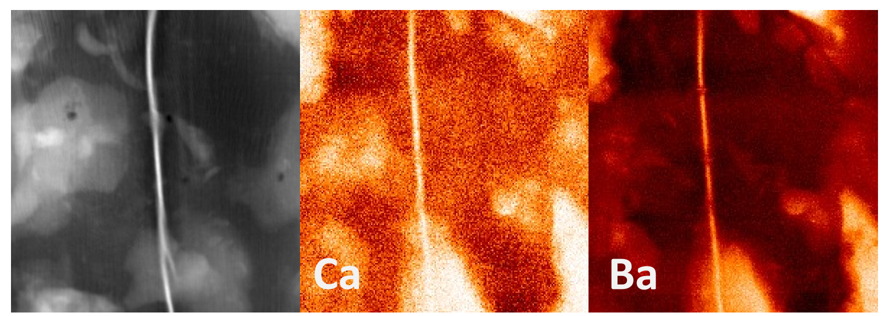
X-ray nano-imaging (ID22NI)

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





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



Les projets ciblés du PEPR-H2

Programme et Equipements Prioritaires de Recherche sur l'Hydrogène décarboné (PEPR – H2)

Production d'hydrogène

CELCER-EHT : Cellules Céramiques EHT durables, performantes et bas coûts

PROTEC : Développement de cellules d'électrolyse à base de céramiques à conduction protonique

Stockage de l'hydrogène

SOLHyd : Stockage solide de l'hydrogène: nouvelles stratégies, nouveaux matériaux

HYPERTSTOCK: Stockage hyperbare de l'hydrogène: référentiel et méthodologies matériaux

Conversion de l'hydrogène

FLEXISOC: Flexibilité des cellules SOC vis-à-vis du combustible

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