Thermomechanical Degradation Behavior of SOFC Materials

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U.S. DEPARTMENT OF ENERGY

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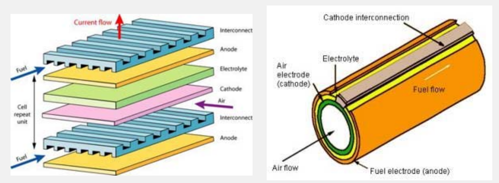
Abstract:

We have developed testing techniques, such as cyclic loading dilatometry (CLD) and creep beam bending (CBB), to measure the thermomechanical properties of individual ceramic components as a function of relative density and microstructure (i.e. porosity and grain size) up to typical processing and operation temperatures. SOFC cathode materials such as LSCF, LSCF-GDC, LSM, LSM-YSZ were analyzed during this study. Material sintering behavior (e.g., shrinkage, warpage, densification) and thermomechanical responses (e.g., viscosity, Poisson's ratio) were determined using CLD and CBB. A thorough understanding of the viscoelastic behavior of these systems over the range of processing and operational temperatures will enable prediction of the mechanical and microstructural stability of SOFCs and accompanying cell efficiency and lifetime.

Introduction and Purpose



- **Research objectives**

Thermomechanical properties of SOFC materials
- -Strain / Strain rate
- -Viscoelastic (E, η)

→ Thermo-mechanical stress model →

Prediction of SOFC system
- -Stress during co-firing and operation
- -Failure/Lifetime
- -Efficiency

- **Prior studies on SOFC sintering stress evolution inform evaluation of thermomechanical degradation**
- **Degradation mechanism of SOFCs**

The consequences of thermal stress and redox cycles lead to performance degradation, limiting SOFC lifetimes.

Thermomechanical / Microstructural / Electrochemical

- Delamination/cracking at interfaces
- Coarsening due to thermal energy
- Thermal expansion mismatch
- Decomposition of cathode/anode materials
- Chemical reaction with electrolyte
- Poisoning (e.g., S, P, As, Cr, etc.)

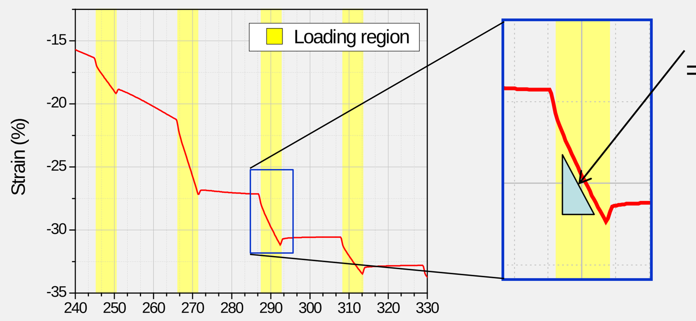
- **Thermomechanical properties of SOFCs**

Thermal stresses induced by mechanical property differences between constituent materials can cause degradation between layers of SOFCs during thermal cycling. By measuring thermomechanical properties such as strain and viscosity of the individual components we can model the stress states in the SOFCs during processing and operation.

Measurement of Viscoelastic Properties by Cyclic Loading Dilatometry (CLD)

- Unique capability which can be used to determine viscoelastic properties (i.e. viscosity, strain and strain rate) of materials as a function of:
  - →Sintering conditions – time, temperature, heating rate, load
  - →Component characteristics - relative density, grain size

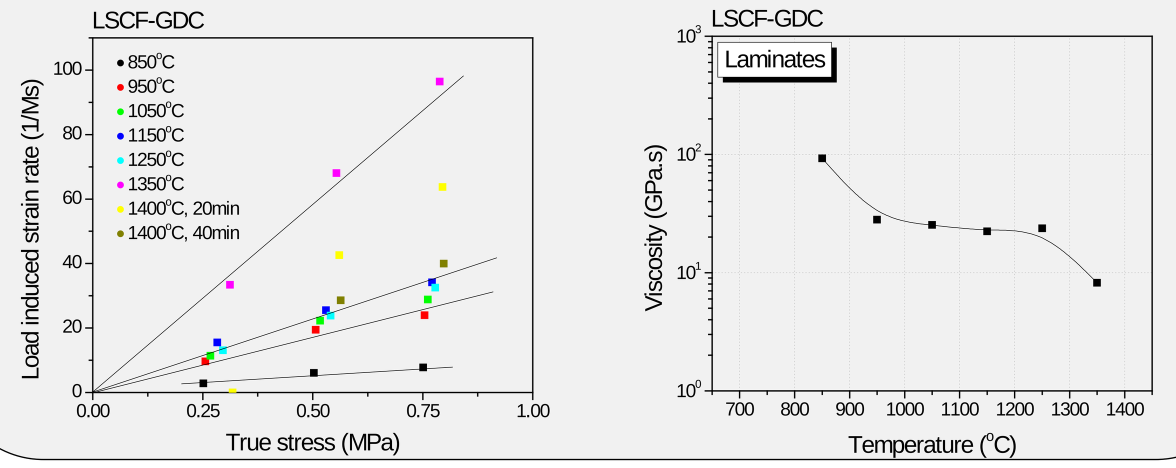
Thermo-mechanical analyzer (TMA)



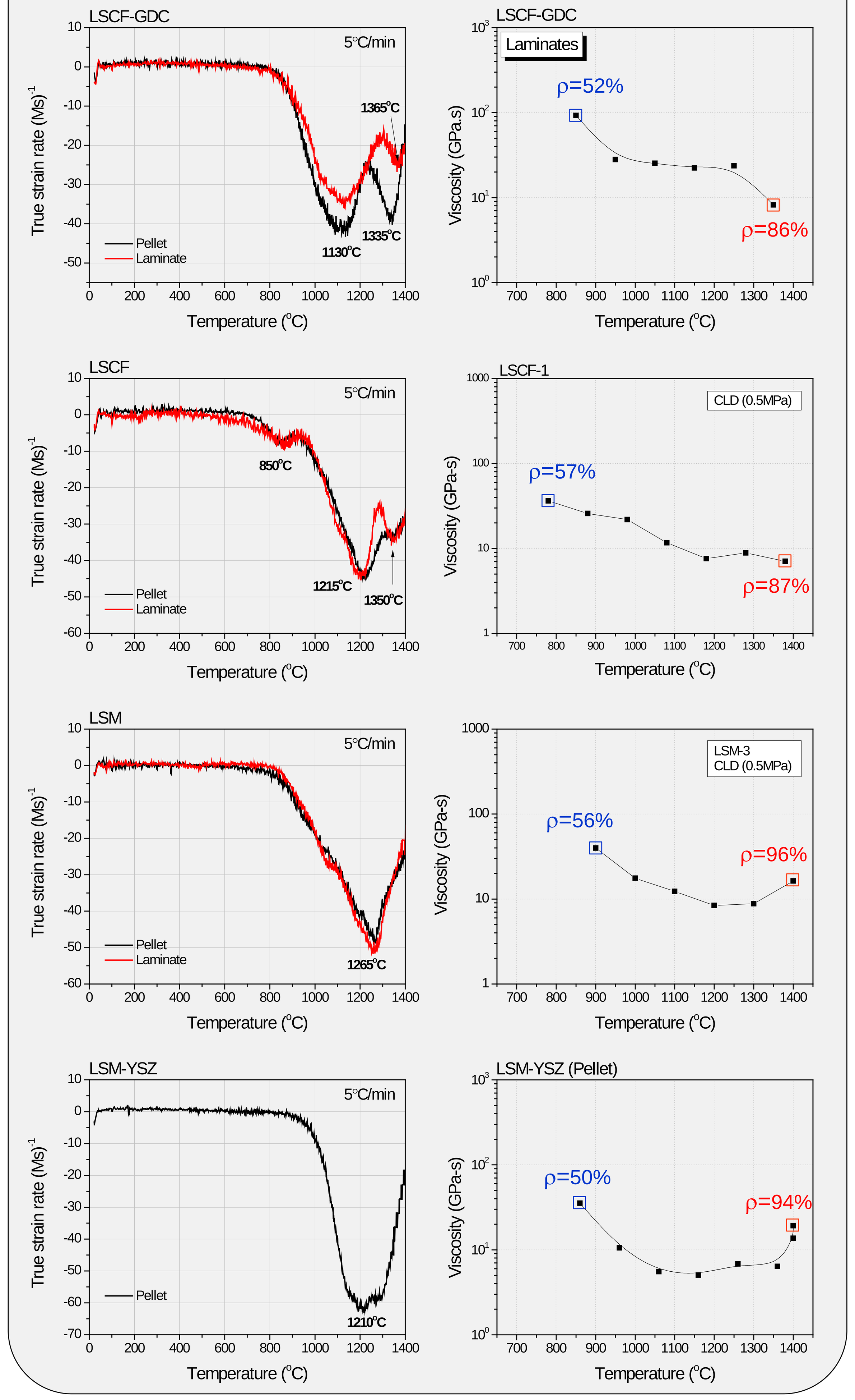
$$\eta = \frac{\sigma_z}{\dot{\varepsilon}_z^t - \dot{\varepsilon}_{zf}^t}$$

Where: $\dot{\varepsilon}_z^t$ is the strain rate under load, $\dot{\varepsilon}_{zf}^t$ is the axial free strain rate, σ_z is applied uniaxial stress, η is uniaxial viscosity

- **CLD of LSCF-GDC**

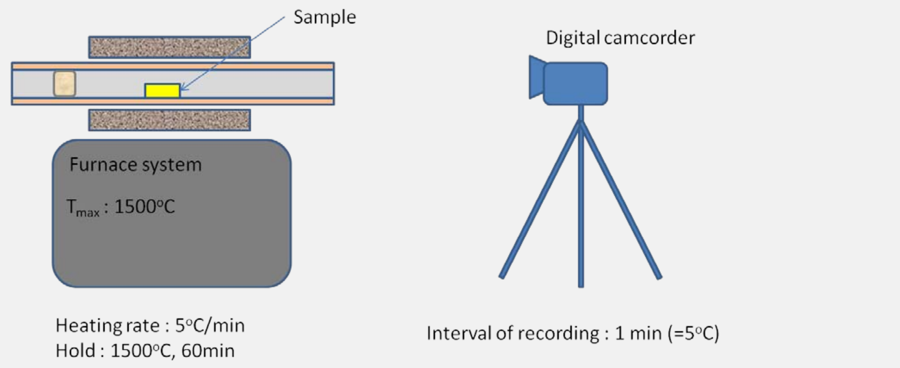


Strain Rate of SOFC Materials During Sintering



Measurement of Viscoelastic Properties by Creep Beam Bending (CBB)

- In-situ observation of creep as a function of:
  - Sintering conditions – time, temperature, ramp rate
  - Loading profile
  - Lamination conditions
  - Material characteristics – composition, relative density



- Deflection Eq. of linear elastic beam (for small deflection dδ/dx < 0.2)

$$\frac{d^2\delta}{dx^2} = \frac{3\rho g(L^2 - 4x^2)}{2Eh^2}$$

$$\delta = Ax^4 + Bx^2 + C$$

$$\delta_{max} = C = \frac{5\rho g L^2}{32Eh^2}$$

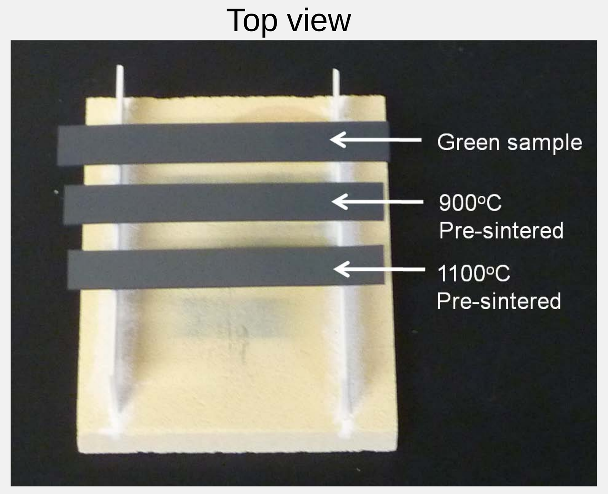
- Linear viscous behavior (during densification process)

$$E_p = \frac{5\rho g L^4}{32\dot{\delta}_{max} h^2}$$

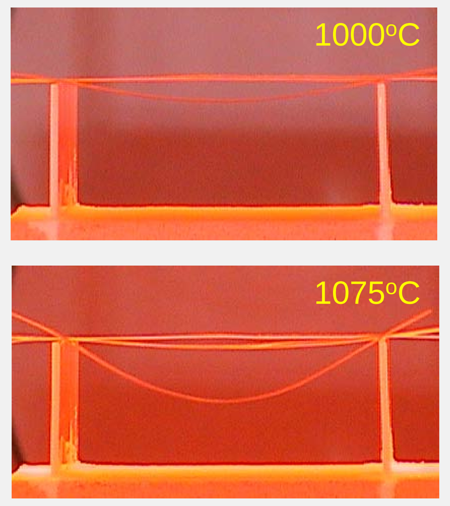
δ: deflection, δ(dot): deflection rate, ρ: density, L: span width, x: distance from center, E: Young's modulus, h: thickness, g: gravitational constant, E_P: uniaxial viscosity

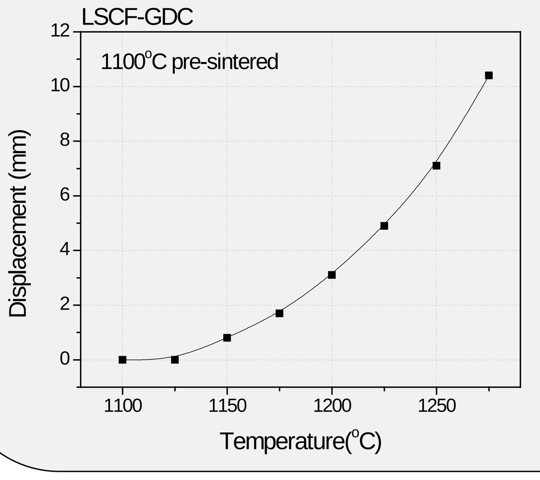
- **CBB of LSCF-GDC**

Top view



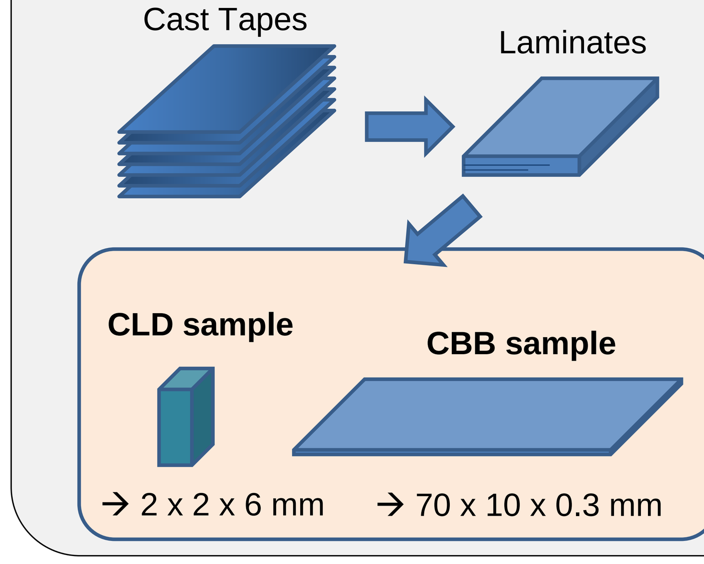
Side view





Temperature (°C)	Viscosity (GPa-s)
1150	21.9
1200	14.0
1250	11.0

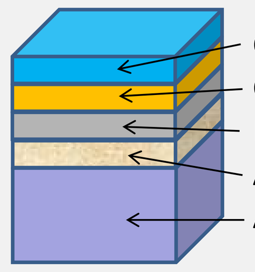
SOFC Fabrication



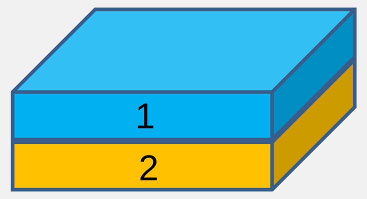
- Cast Tapes
- Stacking
- Uniaxial Pressing (70°C, 10min)
- Lamination (74°C, 30min)
- Binder burn out (600°C, 12h)
- Sample

Stress Model of SOFCs

- SOFC module structure



- Stress between layers



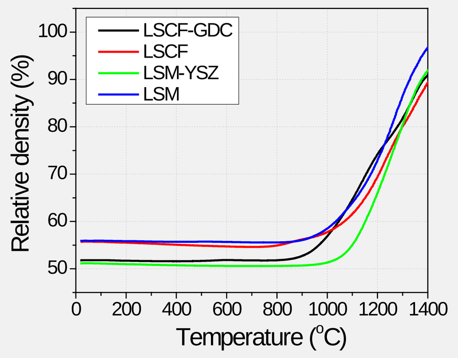
$$\sigma_1(t) = \frac{E_1}{mn+1}\int_0^t \exp\left(-\frac{\lambda_1 + mn\lambda_2}{mn+1}(t-t')\right)\frac{d\Delta\varepsilon(t')}{dt'}dt'$$

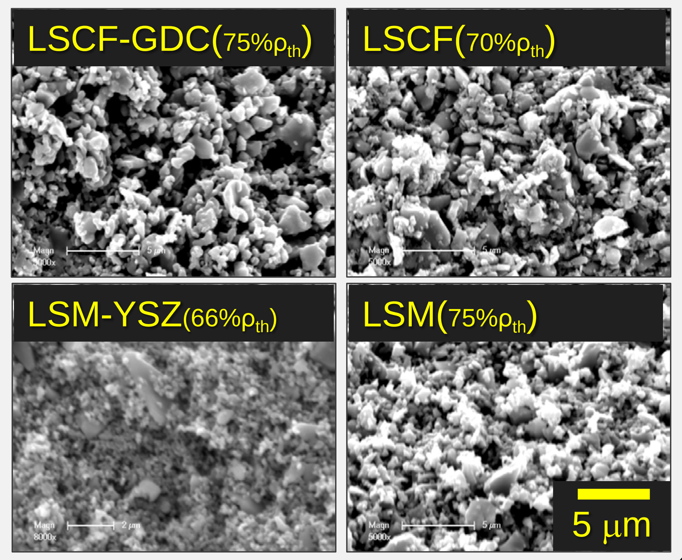
$$m = \frac{x_1}{x_2},\ n = \frac{E_1}{E_2},\ \lambda = \frac{E}{\eta}$$

$$\eta = f(\rho, d)$$

where σ: stress, E: elastic modulus, η: viscosity, t: time, Δε: elastic mismatch, x: layer thickness, ρ: density, d: grain size

Microstructure of SOFC Materials





Summary

- Thermomechanical behavior (strain rate, viscosity) of tape cast SOFC materials was investigated using CLD and CBB.
- At 1150°C, the viscosities of the LSCF-GDC, LSCF, LSM, and LSM-YSZ are 21, 14, 20, and 5 GPa·s, respectively.
- The stress states in the SOFC stacks will be evaluated with the stress model using the measured thermomechanical properties (i.e., strain, viscosity, modulus) of the individual materials.
- Degradation processes will be evaluated by measuring viscoelastic properties as a function of operating conditions (i.e., time, temperature, atmosphere) .

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Disclaimer

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