Standard Operating Procedure

(SOP)

Mechanical Property of SOFC Materials

Test ID: HTE-P-15

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation

Outline/Table of Contents

1. Title Page

In SOFC/SOEC R&D progresses, mechanical properties are another important information but often are downplayed until moving from button cells in research labs to large scale or stacks for manufacturing. This is because the strength issues are often less of a concern when sample sizes are small where the flaw sizes are also small, and this leads to reasonable higher strength for smaller samples. However, this tolerance will be lost when moving towards large size cells or stacks where the strength of brittle ceramics typically decreases, due to higher population of defects. And the importance of mechanical properties arises where structure modelling involves estimation of residual stresses from CTE mismatch, transient stresses from temperature gradient across samples, or thermal shock etc., are all heavily dependent on these mechanical properties to calculate. In this document, we will focus on elastic modulus (Young's and shear's modulus), flexural strength, and Weibull modulus of SOFC cell materials (i.e., anode, electrolyte, cathode, and contact) since these ceramics are generally the weakest in a SOFC stack. It needs to be noted that the mechanical properties of brittle ceramics often are not intrinsic but highly dependent on microstructure (pore, size/distribution, shape and orientation), sample dimension, and test environment and methods. It needs to be noted that there exist no accepted standards (like ASTM) regarding the mechanical property of SOFC cell materials. This is because the very nature of high porosity of typical cell materials. For example, the electrode, electrode support, and contact ceramics often contain large fraction of porosities (~30 to ~50%) such that consistent results are difficult to repeat even with the materials of the same compositions but differs in microstructure. The proposed method in this document is therefore intended to offer a convenient and economical way to measure mechanical properties.

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3. Procedures

The following procedures are to measure the mechanical properties of SOFC materials. Only mechanical properties of elastic modulus (Young's and shear modulus, Poisson's ratio), flexural strength, and Weibull modulus are covered in this document.

3.1 Elastic Modulus

a. Scope and Applicability

Elastic properties of Young's modulus, shear modulus, and Poisson's ratio are important mechanical properties, essential for SOFC engineering design and structure modelling to calculate stresses either from CTE mismatch, transient from temperature gradient, or load carrying capability etc. The traditional method to obtain Young's or shear modulus of a material is by stress-strain curve [1], if it behaves linear elastic. This method presents great challenges to SOFC cell materials due to the very low fracture strain of brittle ceramics (i.e., ~0.1%) such that mechanical tester needs to have high resolutions and accuracy in measuring very small displacement. In addition, the weak and fragile nature makes the sample grip difficult to apply, especially on the highly porous electrode and/or contact materials since it requires machining which can easily introduce large surface defects and hence makes the test results not representative. And finally, the test is destructive in nature where the sample may be lost or unfit for other tests. As a result, pulse-echo method is proposed as the means to measure elastic properties of young's and shear modulus (Poisson's ratio can then be calculated) [2,3]. This method offers many advantages compared to other techniques. First, it is of non-destructive in nature and sample can be used for other purpose. Secondly, it requires minimum machining. For example, no machining is required at all for tape casted anode support like NiO/YSZ where thickness is constant. Third, variable sample sizes can be used with minimum investment in equipment and fast results. For other materials such as cathode contact and cathode where they are typically screen printed on bilayers, one can use the same fabrication process (i.e., tape casting and lamination) to mimic the microstructure and with reasonable thickness of ~500-~700 microns (instead of ~30 microns as in a typical cell) to apply current method. It needs to be pointed out that there are many empirical equations to estimate the elastic properties from fully dense samples and known porosity; however, the large porosity (~30-50%) in typical cell materials often renders the estimation from empirical equations large errors, and therefore not recommended.

b. Summary of Method

The proposed method (pulse-echo) is an economic and non-destructive way to measure elastic modulus (Young's and shear modulus) of SOFC materials at room temperature up to a few hundred ^{o}C (e.g., ~300^{o}C depending on the transducer material). It typically uses a piezoelectric transducer which converts electrical pulses to mechanical vibrations (waves) and the conversion of returned mechanical vibrations (waves) back into electrical energy which is recorded on an oscilloscope as repeating peaks with diminishing intensities. One can then accurately measure the time between peaks and determine the

sound velocity through the thickness of the sample and calculate either the Young's modulus if the wave is longitudinal or shear modulus when it is transverse wave with known sample bulk density and thickness. This method has been applied to typical tape casted NiO/YSZ anode support with porosity up to ~40% [2]. At higher porosities, the attenuation of signals may be significant such that clear identification of repeating peaks may be difficult. Nevertheless, this method is fast and convenient with minimum requirement of sample machining if it is reasonable flat with uniform thickness.

c. Definitions

SOEC – solid oxide electrolysis cell
SOFC – solid oxide fuel cell
LSCF – lanthanum strontium cobalt ferrite
LSM – lanthanum strontium manganate
YSZ – yttria-stabilized zirconia

d. Health & Safety Warning

Only trained person should be operating the test rig. Appropriate safety measures for remediation of hazard and risks associated with powders and solvents, electrical equipment, hot surfaces of the furnace, and flammable gas (Hydrogen). Refer to safe working instructions, personal protective equipment guidelines and compliance requirements in your lab.

e. Cautions

Hot surfaces, flammable gases, hazardous chemicals

f. Interferences

g. Personnel Qualifications / Responsibilities

h. Equipment and Supplies

The method requires to have equipment to generate ultrasonic waves in longitudinal and transverse way by using piezoelectric transducer which can work as both the signal transmitter as well as signal receiver. It may also need an oscilloscope with time resolution in nano-seconds range since time for sound wave to travel of thin SOFC/SOEC cell materials is very minute. One would also need to use coupling agent (paste like materials) applied between transducer head and sample surface to minimize signal loss, and often provided by manufacturer. It is anticipated that there is many equipment commercially available which can combine the two units (pulse generator and oscilloscope as in fig. 1) into one.

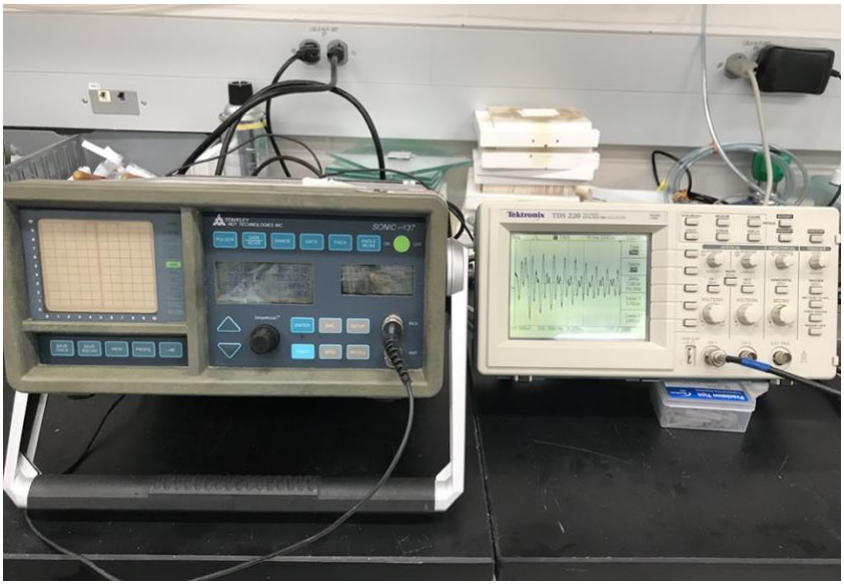


Figure 1 typical experimental set up for measuring elastic modulus where the left is the pulse-echo generator and the right is an oscilloscope.

i. Step by Step Procedure

1. Place the flat sample on a flat dense surface (e.g., flat plate glass or stainless-steel plate to amplify the echo signal)
2. Sample size of 1-inch disk or 1 inch by 1 inch square. Note the sample size should be reasonable larger than the size of transducer. For example, typical transducer is a cylinder of ~1/4 inch diameter such that one can make 4-5 measurements on the 1 inch sample
3. Connect transducer to pulse-echo generator and connect pulse-echo generator to oscillator (note there are many instruments with both functions in one unit so that one may not need the additional oscillator where the peaks can be captured and magnified for precise measurement of time).
4. Turn on both pulse-echo generator and oscillator.
5. Apply appropriate liquid/paste between sample and transducer head so that the signal can be transmitted through the thickness of the sample with minimum loss. (Note each manufacturer may have their own liquid/paste for longitudinal or transverse type of transducer. One can use typical silicon based vacuum grease for longitudinal wave and honey for transverse wave).
6. Press firmly the transducer head on the flat sample (e.g., a glass plate in fig. 2) and adjust the time unit on oscillator so that one can clearly identify repeating signals with equal spacing (time) and diminishing peak intensities (e.g., fig. 3). To minimize edge effect where wave may bounce back and cause difficulties in identifying the correct peaks, the transducer needs to be placed away from the edges.

7. Use 4 to 6 peaks to average the time (t) between two peaks, and 3-5 different locations depending on the size of transducer head to minimize microstructure inhomogeneity. For example, the total time between 6 peaks or peak valley (in Fig. 3) is 1.26 μs and the average time for one round travel of sound wave through sample thickness is 1.26/5 = 0.262 μs.
8. From the time (t) and sample thickness (d), the sound velocity in longitudinal or shear mode can then be calculated as:

$$V_L \text{ (longitudinal in m/s)} = 2d/t \text{ or}$$
$$V_S \text{ (shear in m/s)} = 2d/t$$

9. With known sample bulk density (ρ in g/cc) one can calculate the young's modulus (E), shear modulus (G), Poisson's ratio (ν) as:

$$E = \rho V_L^2(1+\nu)(1-2\nu)/(1-\nu)$$
$$G = \rho V_S^2$$
$$\nu = (1-2(V_S/V_L)^2)/(2-2(V_S/V_L)^2)$$

10. One can use the method to measure elastic properties at temperature up to ~300°C (depending on piezoelectric material's property) ; however, some modification will be required. For example, cable thermal shielding, clamping mechanism to ensure good contact between transducer and sample, and special coupling agent can operate at such high temperatures.

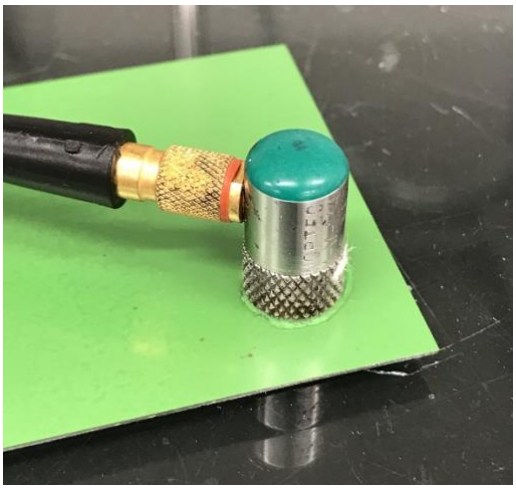


Figure 2. A longitudinal transducer (~0.25 in diameter) is pressed onto a flat SOFC bilayer (NiO/YSZ anode supported YSZ thin electrolyte about 600 micron thick) on the smooth YSZ surface using vacuum grease as coupling agent in between.

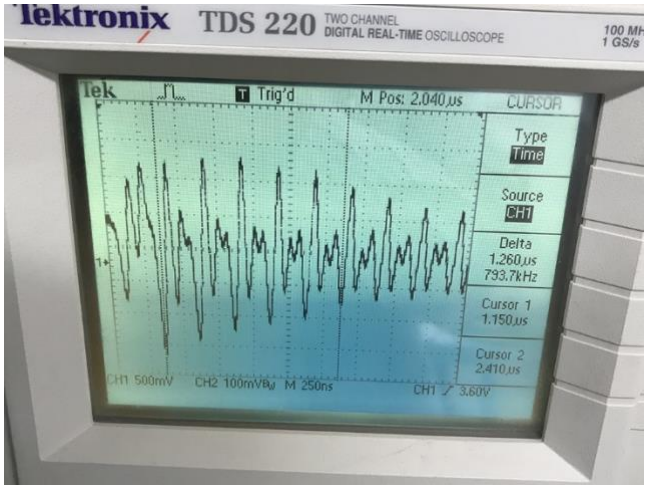


Figure 3 Typical repeating sound waves by transducer and captured on an oscilloscope showing repeating peaks with equal spacing (time). In this example, time cursors are positioned between 6 peak valley and the total time is 1.26 μs so the average time (t) between 2 peaks is 1.26/5 = 0.252 μs.

3.2 Flexural Strength and Weibull modulus

a. Scope and Applicability

Flexural strength is believed to be one of the most important mechanical properties of brittle ceramics, and perhaps more so in SOFC/SOEC applications where a crack of cell is almost certainly will lead to the total failure of the whole stack. This is because the brittle nature of ceramics, the harsh environments in dual atmospheres, and routine thermal cycling where a small crack can continue grow till reaching the its strength. Since the strength of brittle ceramics is microstructure dependent, it is often needed to obtain Weibull modulus whenever flexural strength tests are conducted, if reasonable numbers (e.g., ~30) of samples are available. These two properties are valuable for engineering design in stack development to shed information in life prediction. Flexural strength of ceramics is often measured uniaxially by 3-pt or 4-pt of rectangular bars well machined to desired dimensions and surface finish to minimize machine flaws. However, this is not applicable to SOFC/SOEC cell materials where there exist large porosities and thin in nature, prone to fracture during machining, and will bend substantially such that the equation to calculate strength is no longer valid (out of the linear elastic fracture mechanics). As a result, biaxial flexural test is preferred where no excessive machining and surface finish is required since the maximum stress is at the center or central region, far away from edges. The method has several variations such as piston (or ball) on ring, piston (or ball) on 3 balls, and concentric ring on ring [4-9]. Each method has advantage and disadvantages as discussed in these literatures. And ball-on-ring is selected due to minimum friction effect and low discrepancy (~7%) between experimentally measured slope of deflection vs load and theoretically calculated [9]. Note this method is primarily for planar type SOFC where the cell is flat plate whether it is electrode-supported thin electrolyte or electrolyte supported cell in its as-made form. For tubular type where the

cell is in small tubular shape and flexural strength is to be measured by the conventional 3-pt or 4-pt method.

b. Summary of Method

In the ball-on-ring method, the ceramic thin plate specimen is supported on a ring (or a race of small balls) and loaded centrally with a ball of high elasticity/hardness by a mechanical tester. In principal, a singularity in stress is present with a point loading. In practice; however, the singularity is absent due to local deformation of the loading ball and specimen. A small central region of constant stress was commonly accepted with radius b about 1/3 of the sample thickness. This test rig can easily be constructed with stainless steel for RT application or superalloys/structure ceramics for measuring the strength at elevated temperatures.

c. Definitions
SOEC – solid oxide electrolysis cell
SOFC – solid oxide fuel cell
NiO/YSZ– Nickel oxide/YSZ anode or anode support
LSM – lanthanum strontium manganate
YSZ – yttria-stabilized zirconia

d. Health & Safety Warning
Only trained person should be operating the test rig. Appropriate safety measures for remediation of hazard and risks associated with powders and solvents, electrical equipment, hot surfaces of the furnace, and flammable gas (Hydrogen). Refer to safe working instructions, personal protective equipment guidelines and compliance requirements in your lab.

e. Cautions
Hot surfaces, flammable gases, hazardous chemicals

f. Interferences

g. Personnel Qualifications / Responsibilities

h. Equipment and Supplies

The ball-on-ring test jig can be easily made using stainless steel plates for RT applications, if no commercially products are available (note the commercial product may have a fixed diameter of ring (or race of balls) where for very thin samples the sample may have large deflection before fracture such that the equation to calculate strength may not be valid). It can also be made of superalloys (e.g., Inconel, Hastelloy, or structure ceramics). The base plate (steel) can be machined to 2 in x 2 in x 0.5 in with a machined groove of circle of ~12.5-17.5 mm diameter or machined 12 circular spots (like 1 to 12 o'clock in fig. 4 with diameter about 1/3 of ball bearing) to place 12 ball bearings of same

dimension (e.g., 4.0 mm diameter as in fig. 5). The push rod (e.g., 1 inch diameter) is also machined with a round cavity in the center of one end while the other end can be attached with existing mechanical tester's fixture to precisely record the load. To minimize the tilted loading, a clay material may be placed in the cavity which is slightly larger than the ball diameter so that the load can be self-aligned to be perpendicular applied onto the sample disc. The construction of the test rig can be found in the literatures [4,9].



Figure 4 Typical base plate with 12 machined holes (as in 1-12 o'clock) to form the ring for ball-on-ring test. Diameter of the ring in photo is 17.5 mm.



Figure 5 Typical base plate of ball-on-ring test with 12 ball bearings (diameter of the ball is 4.0 mm).

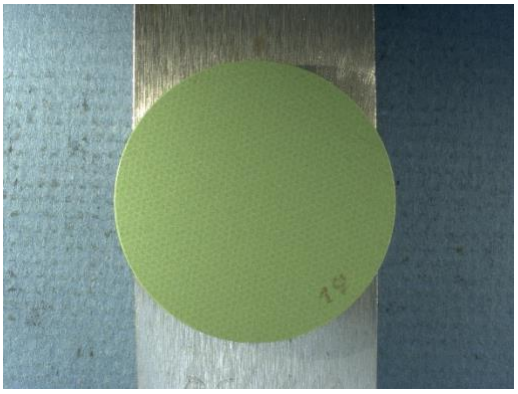


Figure 6 Typical ball-on-ring test with a bilayer disc sitting on top of the ring of ball bearings.

i. Step by Step Procedure

(A) Biaxial flexural strength

1. Put on safety goggle.
2. Place the base fixture with a ring of balls (ball bearing) equally spaced on a circle of 12.5 mm in diameter onto mechanical tester (e.g., Instron or MTS Bionix 400) bench tester with a load cell to 2000 N).
3. Lower the pushrod with a ball at end to align with the center hole of the base fixture (see fig. 4).
4. Place sample disc (with diameter of 20-25 mm) with known thickness on top and center of the base fixture (fig. 6).
5. Lower the pushrod to contact the sample.
6. Start the test with a crosshead speed of 0.5 mm/min.
7. Record the maximum load (P) at fracture
8. Examine the fractured sample to make sure the fracture started from the center of the specimen by reassemble the pieces and trace back to fracture origin. If fracture occurred not from the center, discard the test.
9. For each batch/composition, it'd be better to test 6-10 samples and report the average strength and standard deviation.
10. With known specimen's thickness (t), radius of the support ring (a), radius of the disc sample (R), Poisson ratio (ν), and fracture load (P), the strength (S) can be calculated as [9]:

$$S = [3P(1+\nu)/4\pi t^2] \; x\{1+2[\ln(a/b)]+[(1-\nu)a^2/(1+\nu)R^2][1-(b^2/2a^2)]\}$$

Where b is the radius of the uniform loading at the center and is determined as:

$$b = t \text{ for } \quad z > 1.72\, t$$
$$b = (1.6z^2+t^2)^{0.5}-0.675t \quad \text{for } z<1.724t$$
$$b=0.325t \quad \text{for } z\sim 0$$

and z can be calculated from Hertz elastic contract stress equation between a plate and a ball as:

$$z = (3Pr/4E')^{1/3}$$

where r is the radius of the ball and E' is calculated by

$$1/E' = [(1-\nu_1^2)/E_1]+[1-\nu_2^2]/E_2]$$

Where E is the young's modulus, ν the Poisson ratio, and subscripts 1 and 2 denote the plate and loading ball, respectively.

In the typical ball-on-ring test with condition of $z<<t$, the influence of loading ball radius and the load on the value of b is expected to be very small (<1%) where $b = t/3$ is proposed.

(B) Weibull modulus

For Weibull analysis it is recommend using 25-30 samples to obtain the modulus. Once the strength of these 25-30 samples were determined. The next step is to rank (R) the fracture stress in increasing value and assigns a failure probability (F) to each specimen using:

$$F = (R-0.5)/N,$$

where N is the total number of specimens tested. The empirical two-parameter Weibull equation (assuming unit volume and loading factor) is:

$$\ln \ln (1/(1-F)) = m \ln (S/S_0)$$

where m is the Weibull modulus, S the fracture strength, and S_0 is the characteristic strength. Parameters of m and S_0 can then be determined by plotting ln ln (1/(1-F)) on x-axis versus ln (S) on y-axis that the slope is m and S_0 to be calculated from slope and intercept. An example of RT strength of LSCF4628 is illustrated in the table below and figure 7.

Table 1 Example of Weibull analysis of sintered LSCF4628

R	strength (MPa)	F	ln(strength)	lnln(1/(1-F))
1	2.94	0.0179	1.077	-4.016
2	3.72	0.0536	1.313	-2.899
3	3.91	0.0893	1.365	-2.370
4	4.31	0.1250	1.460	-2.013
5	4.47	0.1607	1.498	-1.742
6	4.70	0.1964	1.547	-1.520
7	4.97	0.2321	1.603	-1.331
8	4.98	0.2679	1.606	-1.165
9	5.05	0.3036	1.620	-1.017
10	5.28	0.3393	1.664	-0.881
11	5.44	0.3750	1.694	-0.755
12	5.63	0.4107	1.728	-0.637
13	5.71	0.4464	1.742	-0.525
14	5.74	0.4821	1.747	-0.418
15	5.81	0.5179	1.760	-0.315
16	5.92	0.5536	1.778	-0.215
17	6.02	0.5893	1.795	-0.117
18	6.08	0.6250	1.804	-0.019
19	6.11	0.6607	1.810	0.078
20	6.46	0.6964	1.865	0.176
21	6.65	0.7321	1.894	0.276
22	7.08	0.7679	1.957	0.379
23	7.13	0.8036	1.964	0.487
24	7.13	0.8393	1.965	0.603
25	7.71	0.8750	2.042	0.732
26	7.95	0.9107	2.074	0.882
27	8.19	0.9464	2.103	1.074
28	9.30	0.9821	2.230	1.393

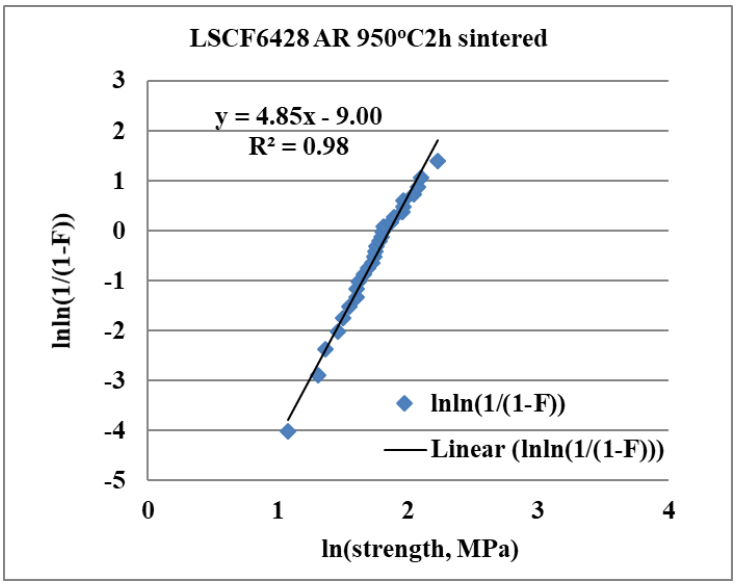


Figure 7 Example of Weibull analysis of sintered LSCF4628 where the slope is the Weibull modulus.

4. Quality Control and Quality Assurance Section

5. Reference Section

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