STRENGTH OF PLANAR CELLS FOR SOFC APPLICATION

J. Malzbender, R.W. Steinbrech and L. Singheiser
Forschungszentrum Jülich GmbH
Institute for Materials and Processes in Energy Systems
52425 Jülich, Germany

ABSTRACT

The mechanical behaviour of SOFC cells with different anode thickness and proprietary microstructural differences is analysed. Bending tests are performed with the surface of the anode either in tension or in compression. Thicker cells are tested using a four-point bending set up, whereas thinner cells are tested using a ring-on-ring loading device. Calculations of the residual stresses within the layers at room temperature show a large compressive stress in the electrolyte. Thus even when a tensile stress is applied to the electrolyte the crack initiates in the anode near the interface with the electrolyte. Hence the modulus of rupture of the anode is determined as the characteristic parameter from the bending tests. Consideration is given also to the effect of the flexural rigidity of the multilayered composite and the distance of the failure origin from the neutral axis. The influence of residual stresses and the effect of the microstructure on the fracture stress are discussed.

INTRODUCTION

The properties of SOFC materials are receiving increasing interest due to the scale up of SOFC cells and stacks and the attempts to improve the long term performance (1). Although the main factors influencing the design are electrochemical in nature (1), the requirement to operate the components at relatively high temperatures and the need for thermal cycling between room and operation temperature makes thermomechanical aspect of the cell components extremely important (2). Since a SOFC cell consists basically of three components, anode, electrolyte and cathode, which are bonded to a composite, residual stresses due to thermal mismatch also have to be considered.

Various investigations on the mechanical properties of SOFC materials exist (3), but the number of studies on specimens from actual cells is limited (4,5). In this paper, an investigation on the modulus of rupture of SOFC cells is presented. Specimens of three planar cell variants with different anode thickness, thin electrolyte and proprietary microstructure and composition are tested.

The modulus of elasticity ($E$) and the modulus of rupture (MOR) can be determined via bending or tensile loading (6,7). The methods are typically applied to isotropic materials using well established relationships (8). However, in the case of layered composites, the determination of $E$ and MOR of an individual layer from the global data obtained in a test is still limited and short of theoretical formulation (9,10). Often the data are analysed on
the basis of the elastic relationships for isotropic materials (11). In the current work equations are provided to determine the MOR of multilayered materials in bending tests.

THEORY

Bending tests are frequently used to determine the elastic moduli and the MOR (6,7,8) of brittle materials. The strain at a position $y$ (Figure 1) is given by (8):

$$\epsilon_y = \frac{P a (y - t_{na})}{2 E I^*} \tag{1}$$

where $P$ is the load, $a$ is the distance between inner and outer loading line, $t_{na}$ is the position of the neutral axis and $(EI)^*$ is the flexural rigidity of the composite beam specimen.

![Figure 1. Four-point bending of a bi-layer specimen (i.e. anode and electrolyte).](image)

Based on the elasticity theory of bi-materials (12), the flexural rigidity of a multilayered composite for bending perpendicular to the interfaces between the layers is (13):

$$\left( EI \right)^* = \frac{w}{3} \sum_{j=1}^{s} \left( \sum_{j=1}^{s} t_j - t_{na} \right)^3 + \left( t_{na} - \sum_{j=1}^{s} t_j \right)^3 \tag{2}$$

where $w$ is the width of the specimen and $t_{na}$ is defined as (14):

$$t_{na} = \sum_{i=1}^{s} E_i t_i \left( 2 \sum_{j=1}^{s} t_j + t_i \right) \left( 2 \sum_{i=1}^{s} E_i t_i \right) \tag{3}$$

In the case of bending of a multilayered plate the flexural rigidity of the plate is (13):

$$\left( D \right)^* = \frac{1}{3} \sum_{i=1}^{s} E_i \left( \sum_{j=1}^{s} t_j - t_{na} \right)^3 + \left( t_{na} - \sum_{j=1}^{s} t_j \right)^3 \tag{4}$$

In SOFC cells, residual stresses also exist due to intrinsic effects (e.g. NiO - Ni reduction) or thermal mismatch. Considering the residual stress $\sigma_{r_{na},y}$ at the position $y$ within the
layer i the fracture stress $\sigma_i$ of the layer i at the position y is obtained from equation [1] as (13):

$$\sigma_{i,y} = \frac{E_i P a}{2EI} (y - y_m) + \sigma_{\text{res},i,y} \quad [5]$$

In the case of a ring-on-ring test the relevant equation (15) becomes:

$$\sigma_{f,y} = \frac{PE_i}{4\pi (1 - \nu_i^2) D} (y - y_m) \left( 1 + \nu \right) \ln \left( \frac{r_2}{r_1} \right) + \frac{1 - \nu}{2} \left( \frac{r_2^2 - r_1^2}{r_3^2} \right) + \sigma_{\text{res},i,y} \quad [6]$$

where $r_1$, $r_2$ and $r_3$ are the radii of the inner and outer loading ring and specimen, respectively. In the case of rectangular plates an equivalent radius is used for $r_3$ (16).

Since in fracture mechanics, $\sigma_f$ is related to the failure-causing flaw size and brittle fracture stresses typically exhibit significant scatter and furthermore depend on the stressed volume or surface area, the data are usually analysed under the assumption of a Weibull distribution of the flaws (Appendix A.1).

**Residual Stress**

In thin multilayer specimens such as unconstrained planar SOFCs the residual stress causes non negligible thermooelastic curvature effects. Accordingly, the residual stress at any position y within a layer i can be determined from the radius of curvature of the sample, since (14):

$$\sigma_{\text{res},i,y} = \left( \frac{1}{r} - \frac{1}{r_0} \right) \left( 1 - \nu_i \right) (y - y_m) + \frac{E_i}{1 - \nu_i} \sum_{j=1}^{n} \frac{E_j}{1 - \nu_j} \int_{r_0}^{r_j} (a_j - a_i) d \theta \quad [7]$$

where the radius $r_0$ is the radius at $T_0$ and the radius is related to the deflection as (17) $r = L^2 / (8 d) + d / 2$. Equation [7] permits, in addition to a consideration of residual stresses due to thermal mismatch, also an assessment of intrinsic stresses via $r_0$. The change in curvature is then determined as:

$$\frac{1}{r} - \frac{1}{r_0} = \frac{1}{D} \sum_{i=1}^{n} E_it_i \left( \sum_{j=1}^{n} t_j + t_i \right) \sum_{j=1}^{n} \frac{E_j}{1 - \nu_j} \int_{r_0}^{r_j} (a_j - a_i) d \theta / 2 \sum_{i=1}^{n} E_i \nu_i t_i \quad [8]$$

Similar formulas for the change of radius due to differences in thermal expansion coefficient can be found in literature (14,18,19,20).

For plates the relationship between radius and residual stress holds only until the out-of-plane deflection becomes comparable to the thickness; beyond this limit the strain and the curvature in the plate are no longer uniform (21,22,23).
**Effect of Coatings on Substrate Fracture**

As an example of how the above equations can be applied, the following situation of a multilayered specimen in a four-point bending is considered. A substrate coated with n layers is loaded with the top-layer in tension. If the substrate fractures at the interface to layer one, position \( y = t_1 \), equation [5] becomes:

\[
\sigma_{t_1,t_1} = E_1 \frac{P_{t_1,t_1} a(t_1 - t_{na})}{2(EI)^*} - \sigma_{na,t_1} \tag{9}
\]

If alternatively the tensile stress is applied to the free surface of the substrate and fracture occurs at this surface, the position is \( y = 0 \) and equation [5] becomes:

\[
\sigma_{t_{1,0}} = E_1 \frac{-P_{t_{1,0}} a(-t_{na})}{2(EI)^*} - \sigma_{na,0} \tag{10}
\]

If the substrate is isotropic, the fracture stresses should be equal: \( \sigma_{t_{1,0}} = \sigma_{t_1,t_1} = \sigma_{t_1} \). Thus, use of the above equations requires either that the residual stresses are determined in advance using equation [7], which needs a measurement of the radius and an exact knowledge of the specimen preparation, or that only the residual stress in the neutral axis is known in advance, which can be determined using equation [7].

**EXPERIMENTAL**

Three anode supported SOFC cell variants from different suppliers, which are termed subsequently A, B, C have been investigated. All designs consisted of a porous Ni-YSZ cermet anode (thickness A ~ 0.27, B ~ 0.55, C ~ 1.5 mm) which supports a co-fired YSZ electrolyte film (thickness ~ 10 \( \mu \)m) and a porous lanthanum strontium manganite (LSM) cathode (thickness ~ 60 \( \mu \)m). The cutting of the samples was performed using either a water jet technique or a conventional diamond saw method. Care was taken to employ the saw always to the side of the sample not to be tested in tension. Thereby the effect of the cutting damage on the measurement of the MOR was limited. The bending tests were carried out with an Instron 1362 testing machine. Specimens of variant A were analysed using four-point bending equipment, whereas the thinner specimens of variant B and C were analysed in a ring-on-ring set up. Although common values for the thermal expansion coefficients of SOFC materials can be found in literature (24), the differences between the materials necessitated the need to measure the difference in thermal expansion coefficient between anode and electrolyte. Mismatch data determined from the thermoelastic bending tests are given in Table 1 for the variants A to C.

| \( \Delta \alpha / 10^{-6} \text{ K}^{-1} \) | A         | B         | C         |
|-------------------------------------------|-----------|-----------|-----------|
| oxidised                                  | 1.5 ± 0.2 | 1.84 ± 0.02 | 1.94 ± 0.07 |
| reduced                                   | 2.34 ± 0.01 | 2.2 ± 0.4  | 2.3 ± 0.1  |

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The elastic moduli of the individual layers, i.e. anode, cathode and electrolyte, have been determined using a depth sensitive Vickers indenter. The elastic modulus was determined on the basis of the unloading curve as outlined in the literature (25).

For the indentation and bending experiments, the average elastic moduli are considered based on a Gaussian distribution (26), whereas the MOR values are analysed on the basis of extreme value statistics after Weibull (27).

RESULTS AND DISCUSSION

An example for the residual stress situation in a variant B cell at room temperature is shown in Figure 2. It can be seen that the electrolyte is under large compressive stress (~400 MPa), which renders crack initiation in this layer unlikely. Due to the residual compressive stress and fracture toughness of the electrolyte, cracks that might initiate in the cathode will not penetrate the electrolyte. Thus it can be concluded that even if the surface of the electrolyte is under tensile stress due to the externally applied moment, the fracture will occur in the anode.

![Figure 2. Example of the residual stresses in a SOFC cell (variant B).](image)

In the bending test lower fracture loads are measured for the anode in tension compared to electrolyte in tension (RT, oxidised cells) independent of the anode thickness (Figure 3). In the case of the oxidised cells at 800°C and reduced anodes (at RT) the MOR ratios differ to a smaller extent from unity. The measured deviations are related to the differences in residual stress, flexural rigidity and position of neutral axis. In fact, if the MOR is calculated from the fracture loads by using the theoretical multiplayer approach, as outlined before and elaborated in more detail in (13), the differences between anode and electrolyte in tension become negligible. However, the anodes of the three variants are not identical with respect to microstructure, which is reflected by the differences in the MOR values (Fig. 4).

On average the MOR of variant C is at least a factor two higher than that of variant A, and the MOR of variant B is below that of A, except for the 800°C results.
Considering that the failure of the brittle anode is governed by the Griffith instability criterion of fracture mechanics, the strength ranking can also be related with the critical flaw (defect) sizes. Assuming that the fracture toughness $K_{IC}$ for variant A, B and C anodes is the same, the ratio of the average flaw sizes $c$ can be calculated since $K_{IC} \sim \sigma \sqrt{c}$. The average critical flaw size is larger for variant B anodes than variant A at RT (oxidised and reduced), whereas the values at 800°C are similar (Figure 5). Corresponding to Fig. 4 the anode of variant C has a significantly smaller average flaw size than variant A and B.

However, the mechanical reliability of the SOFCs depends not only on a high average MOR-value, but the scatter of the fracture stresses has to be low also, i.e. a narrow distribution of the flaw sizes is equally important. The distribution of the failure causing defects can be assessed via the Weibull modulus ($m$). The average $m$ values determined by considering all MOR - measurements (oxidised, reduced, RT, HT) are given for each variant in Table 2.
Figure 5. Normalised average flaw size for the anodes for variants A - C.

Table 2: Average Weibull moduli.

|                | A     | B     | C     |
|----------------|-------|-------|-------|
| Number of      | 63    | 76    | 20    |
| measurements   |       |       |       |
| Weibull modulus, m | 11 ± 1.4 | 7.8 ± 0.9 | 6.2 ± 1.4 |

A larger Weibull modulus is an indication of a narrower flaw size distribution. The data in Table 2 suggest that the flaw sizes in variant A anodes exhibit the smallest scatter.

The probability for failure depends on the stressed area or volume (depending on the failure origin). In the bending experiments the area under tension typically had a size of $A_s = 100$ mm$^2$. If larger cells are used in a SOFC stack the characteristic fracture stress decreases. With the equations given in the appendix the reduction in fracture stress can be calculated. Figure 6 displays the decrease as a function of the Weibull modulus and ratio of the stressed area $A$ to $A_s$.

Since a relatively small area was tested in the bending experiments it can be concluded from Figure 6 that for larger cells (e.g. $200 \times 200$ mm$^2$) the fracture stress can decrease by up to 40 % for variant A, and 60 and 70 % for variants B and C, respectively. Thus the higher MOR of C from tests with small specimens is partly compensated in large cells by the influence of the lower Weibull modulus.
CONCLUSIONS

The mechanical behaviour of SOFC cells with different anode thickness and proprietary microstructural differences has been analysed based on the theory for the bending of multi-layered composites outlined above. Bending tests with the surface of the anode either in tension or in compression yielded a single value of the MOR of the anodes via elimination of the effect of the change of neutral axis, flexural rigidity and residual stress imposed by the layered arrangement of the cells. The MOR of the anodes suggests that through variation of the microstructure, anodes with superior strength can be obtained. But in addition the cells should have a high Weibull modulus, since in larger cells a relatively low $m$-value of the anode leads to a significant reduction in strength.

APPENDIX: FAILURE STATISTICS

The scatter of MOR reflects the size distribution of flaws. Experimental data are usually analysed using Weibull statistics (28): $P(\sigma_f) = 1 - \exp(-\sigma_f / \sigma_{f0})^m$ with the characteristic MOR $\sigma_{f0}$ and the Weibull modulus $m$. As the mean rank estimator, mostly the experimental failure probability relationship $P_i = (i - 0.5)/n$ (29) is used. The characteristic MOR $\sigma_{f0}$ can be determined as the strength at a probability of zero divided by the Weibull modulus $m$ (30,31).

A mathematically more accurate analysis of the data can be based on a maximum likelihood estimate (30,31). This requires the determination of a maximum likelihood parameter $\hat{m}$ via a solution of the non-linear equation (32):
where \( N \) is the number of measurements. The characteristic MOR \( \sigma_{f,0} \) can then be calculated as (32):

\[
\sigma_{f,0} = \left( \frac{1}{N} \sum_{i=1}^{N} \sigma_{f_i}^{\hat{m}} \right)^{1/\hat{m}}
\]  

[A.2]

The Weibull modulus \( m \) is obtained from the maximum likelihood parameter \( \hat{m} \) via (32):

\[
m = b \hat{m}
\]  

[A.3]

Various formula have been suggested to estimate the parameter \( b \), which depends on the number of samples \( N \), i.e. \( b = 1 - 1.593145 N^{-1.046958} \) (32), \( b = 1/(1 + 2.1049 N^{-1.1}) \) (30) and \( b = 1/(0.9807 + 1.7001(1/\ln(1.0408 N))^{5.9733}) \) (31). The difference between these relationships is less than 1% for \( N > 8 \). Furthermore, it has also to be considered that the actual MOR has to be related to the stressed volume \( V \) or the surface area \( A \), depending on whether volume or surface defects cause the failure. This leads to the dependency:

\[
\frac{\sigma_{f_0,1}}{\sigma_{f_0,2}} = (V_1/V_2)^{-1/m} \quad \text{or} \quad \frac{\sigma_{f_0,A_1}}{\sigma_{f_0,A_2}} = (A_1/A_2)^{-1/m},
\]

where \( V_1, V_2 \) and \( A_1, A_2 \) are the different volumes and areas, respectively.

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