

# Spherical indentation of bilayer ceramic structures: dense layer on porous substrate

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## Abstract

Spherical indentation of thin 8YSZ ceramic layers on porous substrates (NiO/Ni-8YSZ) was studied. Indentation-induced elastic and plastic deformation and damage of the bilayer was experimentally analysed. FE simulations of the indentation process were carried out using the Gurson model to account for densification of the porous substrates. The simulated load-depth responses were in excellent agreement with the measured ones. The resulting stress distributions showed that the damage to the YSZ initiates in a tensile region near the interface due to bending during loading at a failure stress of  $\sim 2$  GPa, which is consistent with pores of  $\sim 1 \mu\text{m}$  size seen in the YSZ. Delamination occurs on unloading due to the elastic recovery of YSZ being greater than that of the substrates at a de-bonding stress of 120 MPa. Residual compressive stress in the YSZ inhibits crack opening displacements normal to the layer plane which is beneficial for application of these structures in SOFCs.

**Keywords:** Bilayer structure; Porous ceramic; Spherical indentation; Deformation; FEM

## I. Introduction

Bilayered ceramic structures, whether consisting of a dense layer on a dense substrate, a porous layer on a dense substrate or a dense layer on a porous substrate, are widely used in a variety of applications. One such application is in solid oxide fuel cells (SOFCs) [1] which, regardless of their detailed configuration, have a porous cathode layer and a porous anode layer with a dense electrolyte layer in between. It is of great importance to estimate the reliability and durability of laminated ceramic systems such as SOFCs, through detailed understanding of their mechanical performance and in particular the ability of the different layers to sustain mechanical stresses. These can arise from external mechanical loading and constraints, temperature gradients, and differences in thermal expansion coefficients [2-4]. One common cause of stress in an SOFC is the local load where a ridged metallic interconnector (bipolar plate) makes contact with a porous electrode, or electrode current collector. The loading has to be sufficiently high for the ridge on the interconnector to penetrate into the electrode structure in order to make good electrical contact, but yet not be so high as to damage the dense electrolyte under the electrode. Compared to free standing bulk materials, complexity arises when analysing these layered ceramic structures under mechanical loading, as the thicknesses and layer-to-layer interfacial interactions must also be considered.

In our previous studies [5, 6], we have both experimentally and numerically investigated the elastic and plastic deformation, and damage processes of a typical porous bulk  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) SOFC cathode material possessing a wide range of porosities (4-45%) undergoing spherical indentation. The models developed in these studies take into account the porosity and local densification under the indenter and have proven to be capable of reliably predicting the elastic and plastic deformation and eventual local fracture of the material. We have also applied this same combined experimental and numerical approach to porous thin LSCF films deposited on a dense hard gadolinia-doped ceria (CGO)

substrate [7]. The approach fully accounted for the additional complications arising from the substrate and residual stress, and the simulations showed excellent agreement with the experiments.

The aim of the present work is to apply this methodology to a bilayer comprising a hard dense electrolyte film deposited on a porous anode substrate, before and after reduction, which is a common structural component found in SOFCs and particularly in anode-supported SOFCs. The elastic and plastic deformation of the bilayer was studied together with the critical conditions for damage to the electrolyte. In a future study, the methodology and results will be used to evaluate the effects of local loading on multilayer structures such as complete SOFCs.

## II. Experiment and Simulation

### 2.1. Spherical indentation experiments

Typical SOFC porous NiO-8YSZ anode substrates (oxidised condition), approximately 500  $\mu\text{m}$  thickness with a 10  $\mu\text{m}$  8YSZ electrolyte on one side, were supplied by Jülich IEK-1, Germany. In order to study the specimens with the anode in the reduced condition, some of the as-received specimens were reduced in flowing 92% $\text{N}_2$ /8% $\text{H}_2$  gas by heating to 900  $^\circ\text{C}$  at a rate 3  $^\circ\text{C}/\text{min}$ , holding for 3 h, and then cooling to room temperature at a rate of 5  $^\circ\text{C}/\text{min}$ . As a result, the anode substrates were fully reduced to Ni-8YSZ and in a similar condition to substrates in practical application that are reduced *in-situ* on first use.

Both the as-received (oxidised) and reduced specimens were characterised using indentation with a spherical diamond indenter (25  $\mu\text{m}$  radius), at a wide range of peak loads from 50 mN to 10,000 mN, leading to increasing indentation depths. For each peak load five separate indentations were carried out on the same specimen. Each loading and unloading curve was analysed using the conventional Oliver and Pharr method [8] to give apparent indentation hardness and apparent elastic modulus. Data points for these quantities in the figures appearing later are averages of each set of five indentations and the error bars are  $\pm$  one standard deviation. A detailed description of the indentation process can be found in [9]. In order to characterise the mechanical properties of the substrate (in the oxidised and reduced conditions), indentation was also carried out on the reverse side of the specimen, where there was no electrolyte layer. As in our previous work on bulk specimens and porous films [5, 6], the surface and cross-sectional microstructures as well as indentation-induced damage of the specimens were investigated using the FIB-SEM slice and view technique.

### 2.2. Finite element modelling

2D axisymmetric FE models for indentation simulations of the bilayer structures were used as described in [7] and full details can be found in [5, 7]. In brief, a thin (10  $\mu\text{m}$ ) dense layer was built on a porous substrate having much larger thickness (500  $\mu\text{m}$ ) in Abaqus CAE 6.12 environment (Dassault Systemes, USA). The interface between the layers was perfectly bonded (i.e. no delamination or slippage was allowed). It should be noted that there is an additional layer in these cell specimens which is the so-called anode functional layer between the support and the electrolyte. This layer is approximately 5  $\mu\text{m}$  thick and has the same composition as the support, but has a finer, typically sub-micron, microstructure to enhance its electro-catalytic performance. The presence of this layer is neglected in the model as it is expected to have very similar properties to the substrate, since previous work has shown that in similar partially sintered ceramics the main parameter controlling the mechanical properties is the porosity and not the length scale of the microstructure [10].

The nodes along the axis of the indenter were constrained such that only vertical displacements were permitted and the bottom of the substrate was fully constrained. The spherical indenter was modelled as a rigid body with a radius  $R_i$  of 25  $\mu\text{m}$ , identical to the real indenter used in the experiments. Frictionless contact was assumed between the indenter and the electrolyte top surface [11-13]. The materials were assumed to be homogeneous and isotropic with perfect elastic-plastic behaviour. The numerical method developed in our previous study has been shown to be quantitatively accurate in

simulating indentation of porous bulk ceramics and films. In that method we used the Gurson model [14, 15] to simulate the densification behaviour of the porous material in the compressive zone of the indent. In this model the yield condition is a function of the porosity ( $f$ ) and is given by the following expression, Eq. (1),

$$\Phi = \left(\frac{q}{\sigma_y^d}\right)^2 + 2f \cosh\left(-\frac{3p}{2\sigma_y^d}\right) - 1 - f^2 = 0 \quad (1)$$

where  $\sigma_y^d$  is the yield stress of the dense matrix material,  $q$  is the effective von Mises macroscopic stress and  $p$  is the macroscopic hydrostatic stress. Since we apply this relationship outside the limits of its strict validity [14, 15], we treat  $\sigma_y^d$  as an adjustable parameter whose value is obtained by a best fit to the indentation response of the porous substrate (this is not necessarily the same as the yield stress of the dense matrix). Substituting the measured porosity and the fitted value of  $\sigma_y^d$  into Eq. (1) and considering a uniaxial stress state gives a value for the uniaxial yield stress of the porous anode support.

The dimensions of the layer and substrate, the residual stresses in the layer and substrate prior to indentation, and the porosity in the substrate could be specified as needed in the numerical analysis. Adaptive meshing was performed in the regions close to the indenter contact point to improve the resolution of the stress distribution. The loading and unloading parts of the indentation were simulated by stepwise vertical displacement of the indenter into and off the structures.

### III. Results and Discussion

#### 3.1 Indentation-induced damage

The specimens, in both oxidised and reduced states, did not show any detectable cracks or delamination at the interface between layers before indentation. Indentation experiments were first carried out to determine the characteristic mechanical parameters for the porous substrate in its oxidised and reduced states. Indentation experiments were then carried out onto the dense layer of the bilayer with the objectives of reproducing the bilayer loading and unloading behaviour with the FE simulation in the absence of cracking and then, at higher loads, to determine the nature of any damage and the critical conditions for its occurrence.

From the SEM images of the top surface of the electrolyte after indentation (Fig. 1), detectable ring cracks in the indented contact area could be seen when a threshold load was reached. For the oxidised specimen this was between 1800 – 2000 mN before and after the first ring crack was seen, while for the reduced specimen the threshold load fell in the range 1200 – 1400 mN. Thus the threshold loads for damage initiation are  $1900 \pm 100$  mN for the oxidised specimen and  $1300 \pm 100$  mN for the reduced specimen. For loads significantly above the threshold, the cracking of the electrolyte was more severe for the reduced specimen than for the oxidised one as shown in Fig. 2.

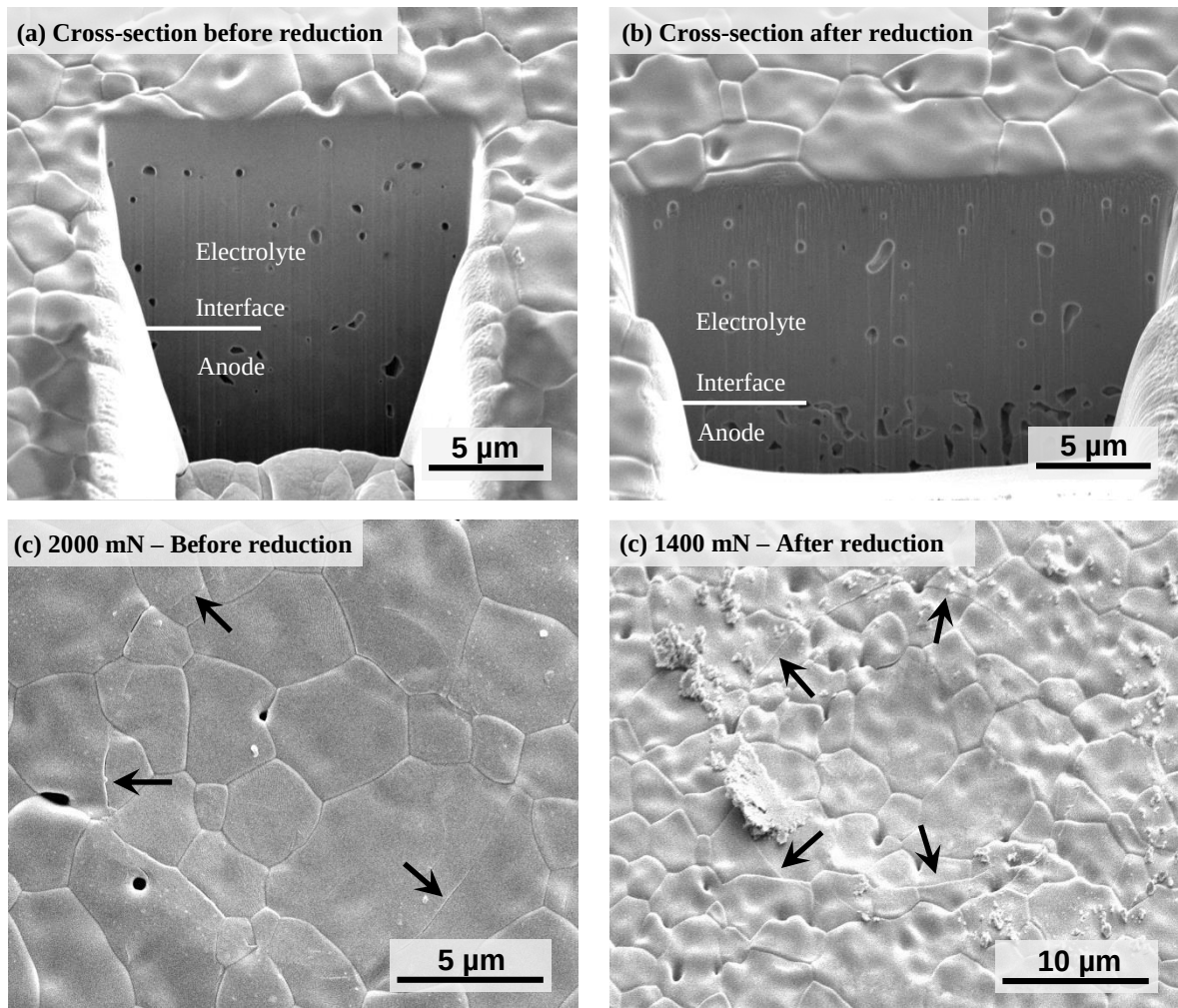


**Fig. 1** Cross-sections and crack features on the top surface induced by spherical indentation of the electrolyte layer for oxidised and reduced specimens. Cross-sections before indentation of (a) oxidised and (b) reduced specimens. Top surface of indented region at the threshold load for the first surface crack to occur (c) after indentation at 2000 mN for the oxidised specimen and (d) after indentation at 1400 mN for the reduced specimen. Arrows indicate ring cracks.

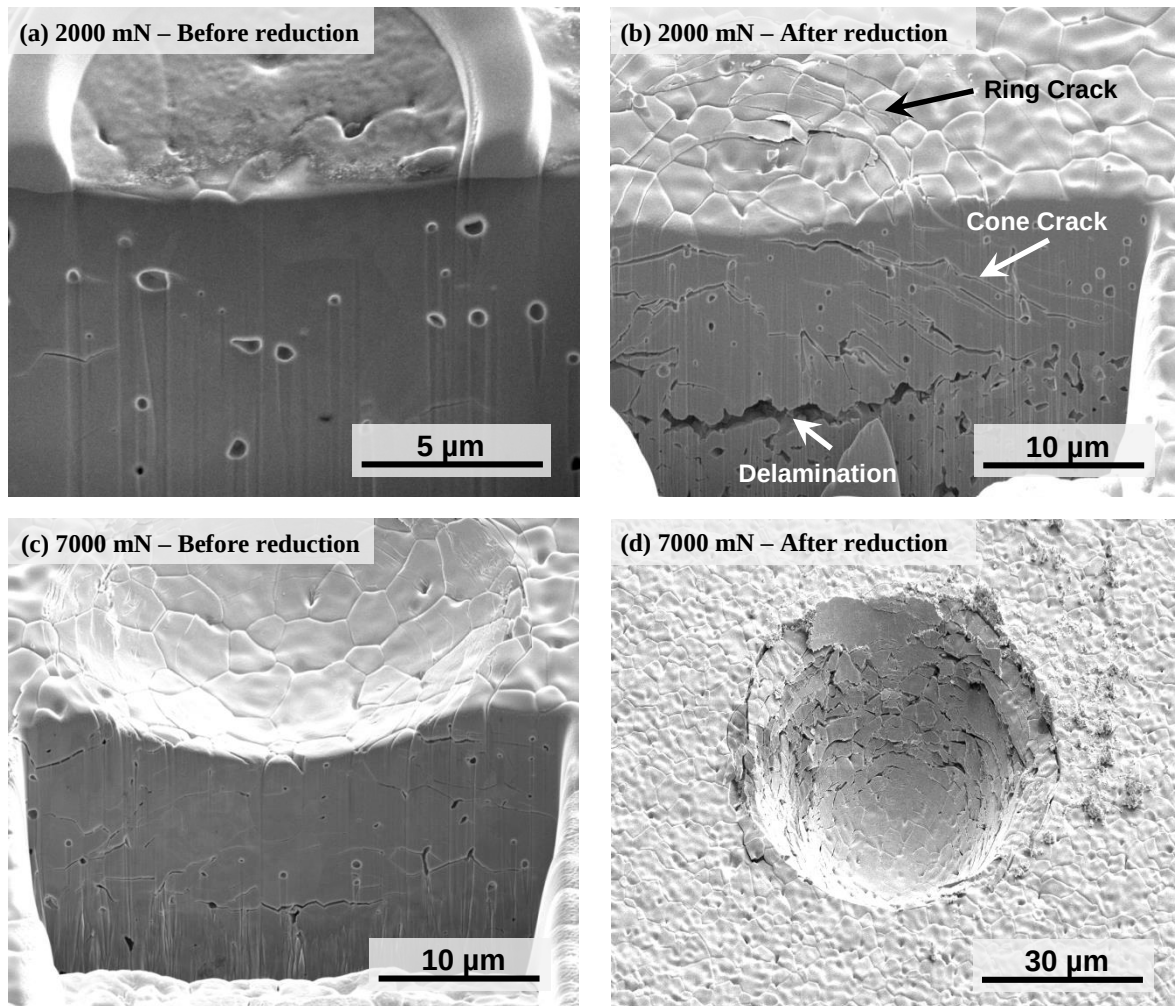


**Fig. 2 Top surface and cross-sectional features of the oxidised and reduced specimens after indentation at similar peak loads. Cross-section after indentation at 2000 mN peak load for (a) oxidised specimen (the ring feature on the top surface is Pt deposited to protect the surface ring crack during milling) and (b) reduced specimen. (c) Cross-section of oxidised specimen and (d) surface of reduced specimen after indentation at 7000 mN peak load.**

It can be seen that after indentation at a peak load of 2000 mN, there is only minor damage to the electrolyte layer in the oxidised specimen (Fig. 2 (a)). The damage takes the form of some short localised cracks at grain boundaries in the YSZ and oriented approximately in the plane of the layer. These internal cracks appear at a similar threshold load to the surface ring cracks. There is very little plastic deformation of the YSZ as can be seen from the shallow residual indentation imprint. Conversely, much more significant damage was generated in the reduced specimen after indentation at the same peak load (Fig. 2 (b)). On the top surface of the YSZ concentric ring cracks are seen and within the electrolyte layer a system of cracks radiating outwards and downwards at an approximate angle of  $30^\circ$  to the plane of the film similar to the cone cracks that can form under certain conditions when a bulk brittle material is subjected to spherical indentation. Finally there is a region of delamination at the interface between the film and substrate with a radius similar to the contact circle. Plastic deformation of the YSZ is also more noticeable for the reduced specimen. When the peak load was increased to 7000 mN for the oxidised specimen, the damage was qualitatively similar (Fig. 2 (c)) to that seen for the reduced specimen after a peak load of 2000 mN, although not as severe (Fig. 2 (b)), in that there are fewer cone cracks and the delaminated region is much smaller than the contact radius. There is significantly more plastic deformation in the YSZ, as would be expected for this higher load. There is also an indication that the ring cracks seen on the surface are not connected directly to the cone cracks. A peak load of 7000 mN on the reduced specimen resulted in severe damage as shown in Fig. 2 (d).

### 3.2. Indentation loading and unloading responses

#### 3.2.1. Mechanical properties of anode substrates before and after reduction

The response curves in Fig. 3 show examples of the indentation load as a function of depth for the indentation experiments on the anode substrates before and after reduction to a maximum load of 400 mN. The application of a given load resulted in much deeper penetration for the substrate after reduction (almost 5 times that before reduction). This is expected since the porosity increases significantly on reduction. The porosities were estimated from image analysis of SEM micrographs to be 14.6% in the oxidised state and 30.1% in the reduced state, and these were used as input parameters in the FE simulations. The loading and unloading curves were analysed using the same procedure as described in previous work [9] to give the elastic modulus and Gurson yield stress for the oxidised and reduced states as summarised in Table 1. The elastic modulus values for the anode substrates are seen in Table 1 to be comparable to those reported in the literature at the same porosity for similar anode substrates.

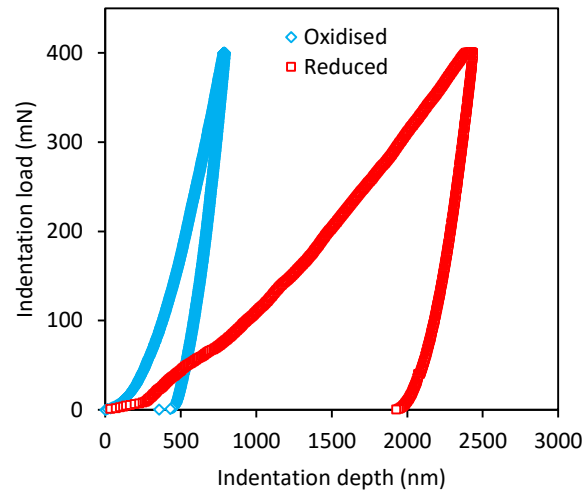


Fig. 3 Indentation load-depth response curves for the anode substrates before and after reduction.

#### 3.2.2. Indentation of electrolyte side of bilayer

Because the electrolyte layer is thin, and the porous substrate is relatively compliant, the indentation response of the electrolyte side is significantly influenced by the substrate. Spherical indentations were carried out at loads ranging from 50 mN to 10000 mN, and the corresponding indentation depths are plotted in Fig. 4. It can be seen that the loading curves for the oxidised and reduced specimens start to deviate markedly from each other (difference greater than two standard deviations) for indentation loads above approximately 600 mN, which is lower than the threshold loads for causing detectable damage. This load reflects the onset of the different contributions from the two types of anode substrate influencing the indentation behaviour of the electrolyte layers. A load of 600 mN corresponds to approximately 700 nm indentation depth, which is 7% of the thickness of the electrolyte layer and is slightly higher than the 5% value normally regarded as the limit for avoiding influence from the substrate. Zheng and Sridhar [16] analyses spherical indentation of an elastic film on an elastic-plastic substrate with an elastic modulus equal to 0.1 that of the film. They conclude that the substrate has no significant effect on the indentation response if the ratio of indentation depth to film thickness,  $h$ , is less than  $h/(4R)$  where  $R$  is the indenter radius. For the present experiments this indicates that the substrate has no influence for indentation depths less than 10% of the film thickness, which is consistent with the present results. The reduced substrate has much higher porosity than in the oxidised state and as a result is significantly more compliant. At the maximum load used (10 N) the indentation displacement becomes approximately equal to the electrolyte thickness (10  $\mu\text{m}$ ) in the case of the oxidised specimen and much greater (over 25  $\mu\text{m}$ , which is the radius of the indenter) for the reduced specimen. These large displacements correspond to highly damaging shear as the region under the indenter is pushed downwards with respect to the surrounding material.

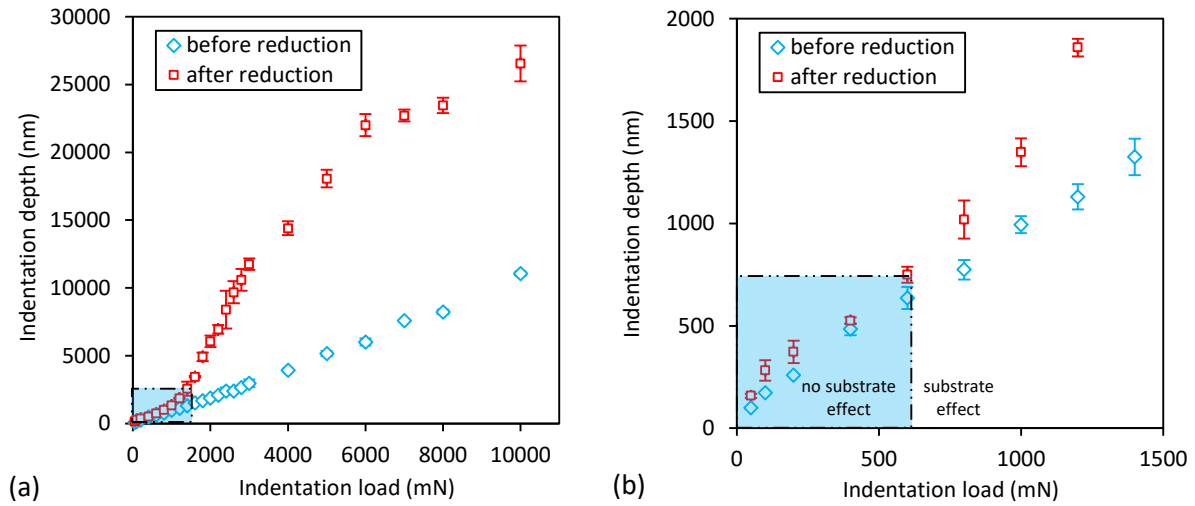


**Fig. 4 (a) The indentation depth as a function of indentation load for indentation of the electrolyte layers in the specimens before and after reduction and (b) the data over a range of small loads shown by the shaded region in (a). The shaded region in (b) indicates the very low load region in which the response is not influenced significantly by the substrate.**

The indentation loading and unloading responses were analysed by applying the Oliver and Pharr method which has become standard for homogeneous bulk materials [8]. This yields an elastic modulus from the unloading curve and a hardness from the load divided by the projected contact area during loading. In the case of bilayer specimens such as the ones in this study, the analysis is not generally valid, but here we use it to produce apparent values of modulus and hardness in order to emphasise the influence of the substrates. Fig. 5 and Fig. 6 show respectively the apparent elastic modulus and hardness determined at each maximum applied load for specimens before and after the substrate was reduced. From Fig. 4 the influence of the substrate on the loading curve, which determines the hardness, is negligible only in the load range below 600 mN (750 nm depth). This is reflected in Figs. 5(b) and 6(b) as a fall-off in apparent hardness for loads above approximately 1000 mN. The increase in apparent hardness with load for lower loads is a characteristic of indentation with a spherical indenter [17] and reflects the properties of the electrolyte layer. From the data in this low load region, the Gurson yield stress for the electrolyte was estimated to be  $\sigma_y^d = 3.8$  GPa. The apparent elastic modulus depends mainly on the unloading curve and from Figs 5(a) and 6(a) is reasonably constant for loads below approximately 800 mN (800 nm depth) for the oxidised specimen and 400 mN (550 nm depth) for the reduced specimen. In both cases this gives an elastic modulus for the electrolyte  $E_e = 200 \pm 10$  GPa, which is close to previously reported results for similar bulk material (193 GPa using the impulse excitation technique [18], and 192 GPa using the pulse-echo method [19].) The deduced mechanical parameters of each component material in the bilayer structure are summarised in Table 1.

**Table 1 Properties of the electrolyte and anode substrate before and after reduction.**

| Component type | Material composition | Porosity (vol%) | Thickness ( $\mu\text{m}$ ) | Elastic modulus (GPa) | Elastic modulus reported in literature (GPa) | Gurson yield stress $\sigma_y^d$ (GPa) | Uniaxial yield stress $\sigma_y^p$ (GPa) |
|----------------|----------------------|-----------------|-----------------------------|-----------------------|----------------------------------------------|----------------------------------------|------------------------------------------|
| Electrolyte    | 8YSZ                 | 5               | 10                          | $200 \pm 10$          | 193 [18]<br>192 [19]                         | 3.8                                    | 3.58                                     |
| Substrate      | NiO-8YSZ             | 14.6            | 500                         | $152 \pm 8$           | 143.5 [18]<br>144.4 [20]<br>145.2 [21]       | 3.0                                    | 2.38                                     |
|                | Ni-8YSZ              | 30.1            | 500                         | $72.7 \pm 1.3$        | 80.3 [20]<br>96 [21]                         | 0.96                                   | 0.67                                     |

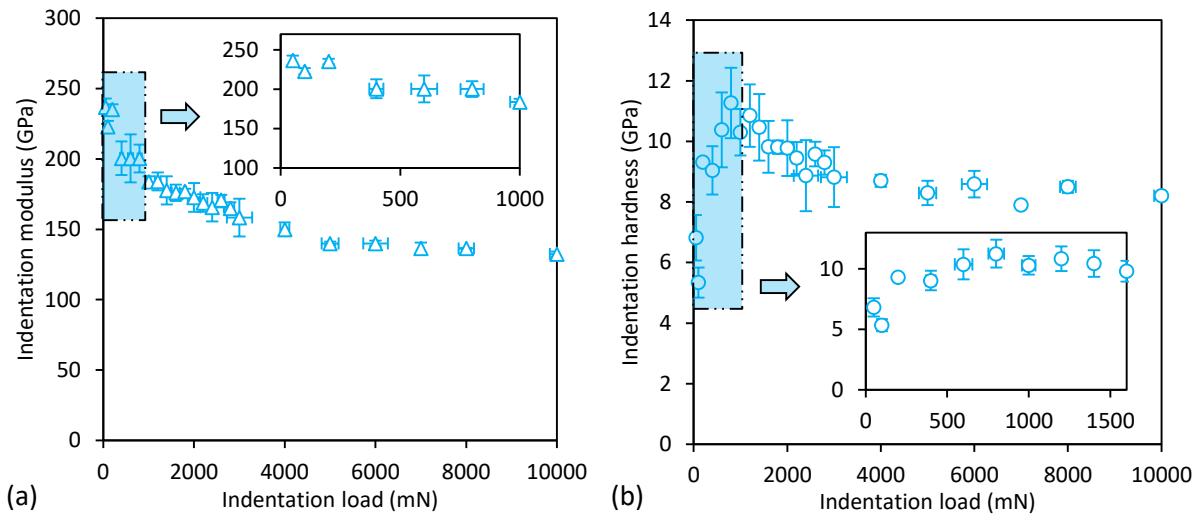


**Fig. 5 (a) Apparent elastic modulus and (b) apparent indentation hardness as a function of indentation load for indentation into the electrolyte layer on the oxidised specimens. Insets are expanded plots over a range of small indentation depths enclosed in the shaded rectangles.**

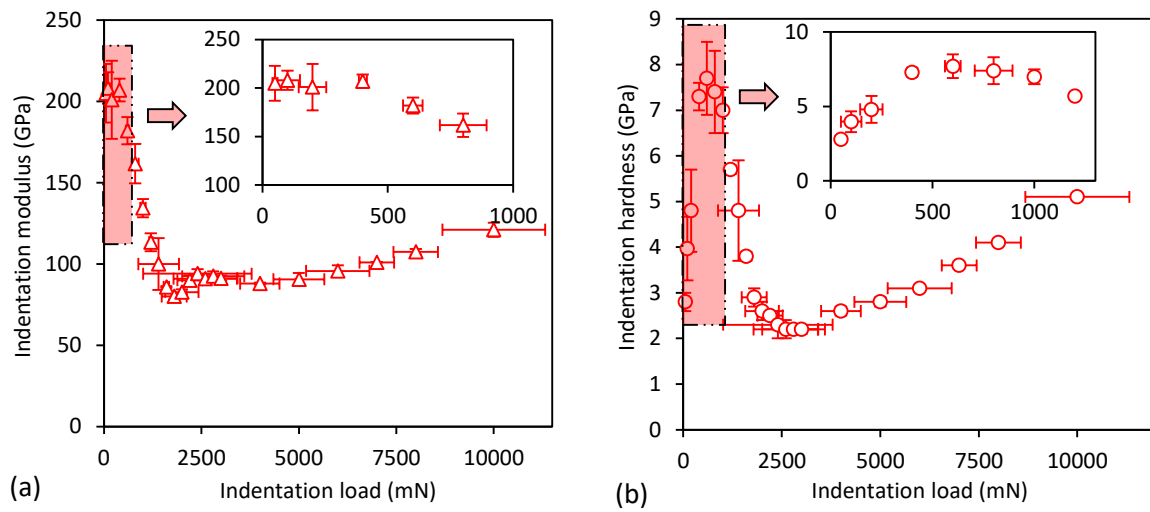


**Fig. 6 (a) Apparent elastic modulus and (b) apparent indentation hardness as a function of indentation load for indentation into the electrolyte layer on the reduced specimens. Insets are expanded plots over a range of small indentation depths enclosed in the shaded rectangles.**

At very shallow indentation depths the response can be influenced by the surface roughness of the specimen. The results for elastic modulus in Figs. 5(a) and 6(a) show no variation at the very shallow indentation depths indicating that the surface roughness is not influencing the results.

As expected from Fig. 4, the apparent elastic modulus and hardness data in Fig. 5 and Fig. 6 are similar and reasonably constant over the small depth range in which the effect of the substrate was negligible. At higher loads the substrates have a major influence and the two types behave qualitatively differently. For the oxidised specimen the apparent elastic modulus and hardness gradually decrease to a plateau, whereas for the reduced specimen the values first drop drastically before gradually increasing at higher loads. This increase at higher loads for the reduced specimen is probably due to a greater degree of densification in the substrate under the indenter for the more porous material. In addition, at these higher loads the electrolyte layers have sustained considerable damage.

The degree of elastic recovery (i.e. the ratio of elastically recovered depth over maximum depth) is shown in Fig. 7 as a function of indentation load. For the oxidised specimen the elastic recovery gradually decreased with increasing indentation load, whereas for the reduced specimen the elastic recovery decreased much more dramatically and soon reached a very low level of approximately 5%. This reflects the easier plastic deformation of the more porous substrate and the greater extent of damage to the YSZ layer on this substrate.

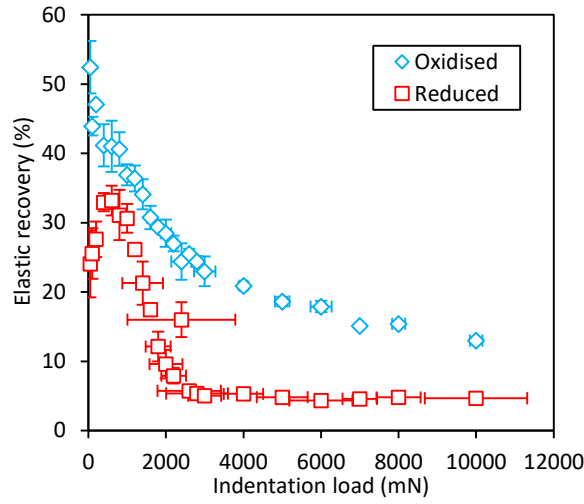


Fig. 7 Elastic recovery (i.e. ratio of recovered depth over maximum depth) as a function of indentation load for oxidised and reduced specimens.

### 3.3. FE simulations

The simulations do not include any damage features and therefore only apply to loads below, or at, the threshold load for damage to first occur.

#### 3.3.1. Effect of residual stress

In-plane equi-biaxial residual stresses in the YSZ layers are generated by the mismatch in thermal expansion coefficient (TEC) between the YSZ and the substrate. For the specimens studied in this work, as the electrolyte has a lower TEC than the anode (before and after reduction), compressive stress is generated in the electrolyte layer upon cooling from the fabrication temperature. The YSZ has a lower TEC (typically  $10.5 \text{ ppm K}^{-1}$ ) than the anode support (typically in the range  $12.5$  to  $13 \text{ ppm K}^{-1}$ ), which puts the electrolyte in compression after cooling to room temperature from a stress free condition at high temperature. This residual stress, in anode-supported YSZ electrolytes that was similar to the current specimens, is reported to be approximately  $-600 \text{ MPa}$  and  $-400 \text{ MPa}$  in the oxidised and reduced specimens, respectively [4, 22, 23]. Since the substrate is much thicker than the electrolyte layer, the balancing tensile residual stress in the substrate is very much lower and is neglected here. In order to explore the effect of residual stress on the mechanical behaviour and the measured apparent elastic modulus and hardness, a range of electrolyte residual stress values in the range  $0$  to  $-1000 \text{ MPa}$  were input into the simulations with a given peak load at  $400 \text{ mN}$ . The simulation results are summarised in Fig. 8.

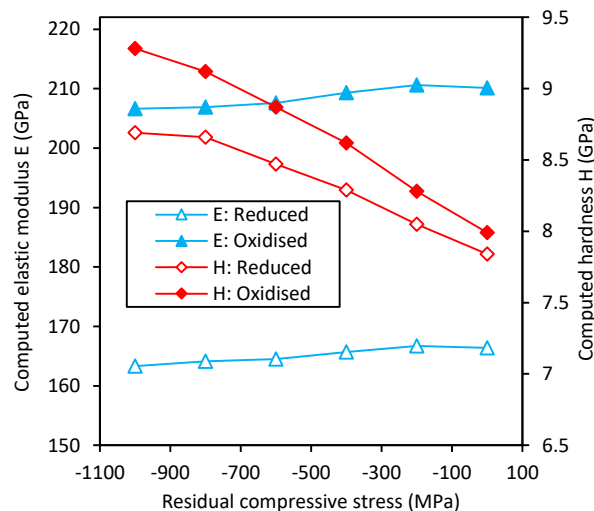


Fig. 8 The effect of electrolyte residual stress on the computed apparent elastic modulus and hardness of the electrolyte layer from the FEM simulations.

The simulations show that the compressive residual stress in the YSZ decreases the apparent elastic modulus by a few percent (1.9 % at -1000 MPa), but increases the apparent hardness by a larger relative amount (approximately 10%). The dependence of indentation modulus on residual stress is small, but a real effect. It is similar, but smaller to that reported in experiments with a sharp indenter for tungsten films on silicon, which showed a change of 10% for a similar range of residual stress [24]. In all the following simulations the experimental electrolyte residual stresses were used; namely, -600 MPa for the oxidised state and -400 MPa for the reduced state.

### 3.3.2. Simulated indentation response curves

Examples of indentation response curves at loads below the damage thresholds are presented in Fig. 9 and demonstrate excellent agreement between the simulated and experimental data for both oxidised and reduced specimens. In the case of the reduced specimen, the loading-unloading loop has a significantly wider shape due to a pronounced negative curvature on loading caused by the easier plastic deformation of the more porous substrate.

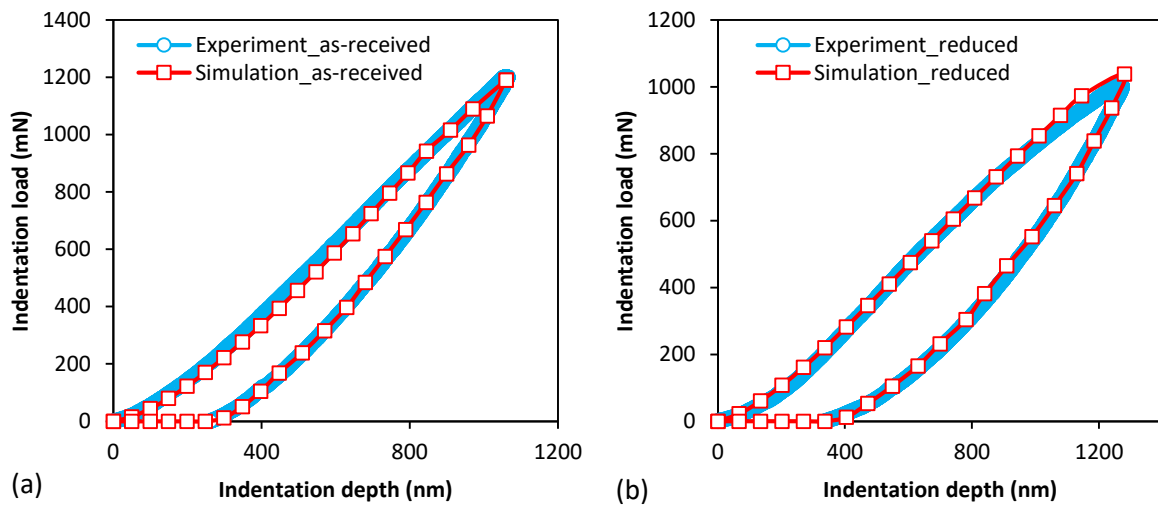
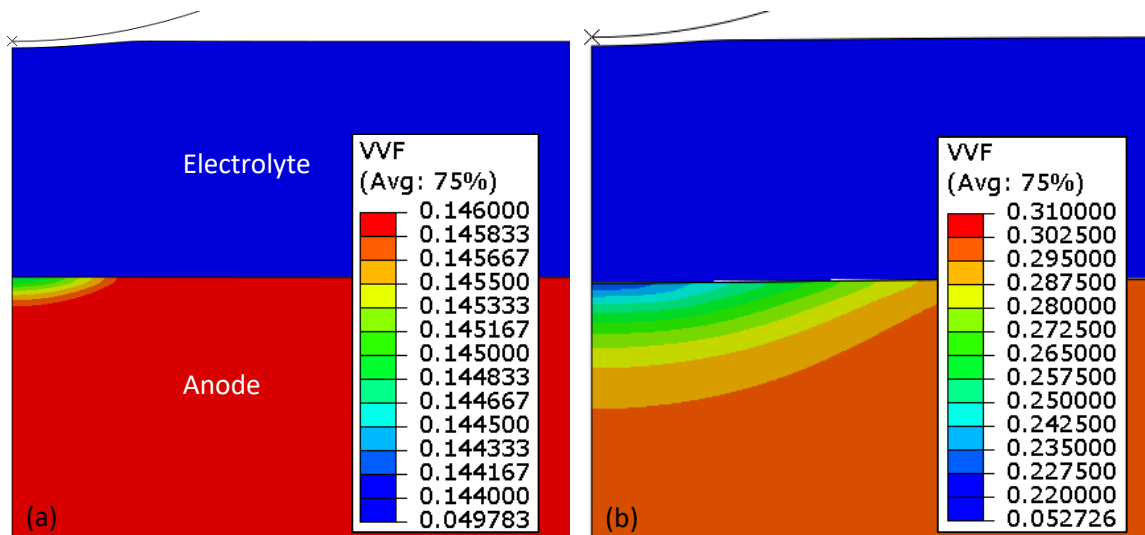


Fig. 9 Comparison of the experimental and simulated indentation response curves for the two types of specimens, (a) as-received specimen with oxide anode substrate and (b) specimen with reduced anode substrate. The values of parameters used in the simulations are those given in Table 1 and the Poisson ratio of all the materials was assumed to be 0.3.

The simulations also compute the local porosity expressed as void volume fraction (VVF) in the anode substrate and examples of these are shown in Fig. 10 for the oxidised and reduced specimens after complete unloading following a peak applied load of 1000 mN. It is readily seen that the reduced substrate shows a larger change in porosity and the change for the oxidised substrate is extremely small and thus considered negligible.



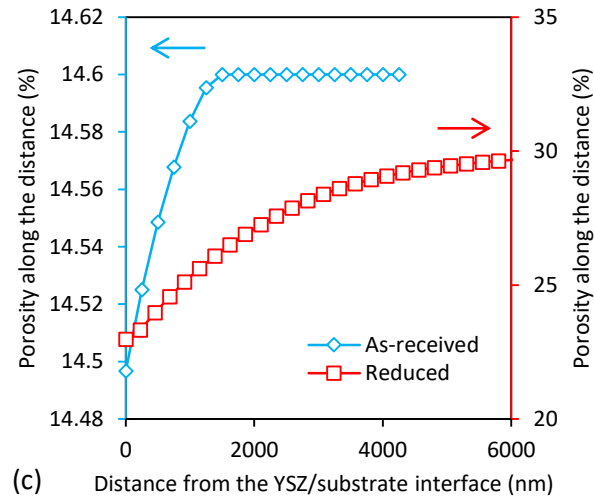


Fig. 10 Porosity changes in the anode substrate calculated by FEM simulation after 1000 mN indentation load was fully removed. (a) Porosity contour plot for the oxidised substrate, (b) porosity contour plot for the reduced substrate, and (c) porosity variation with distance along the central axis of indentation measured from the interface between the substrate and YSZ layer. Note that in (a) and (b) only the upper part of the substrate is shown.

### 3.3.3. Stress analysis and damage processes

The damage caused by indentation at peak loads above the threshold, as revealed in the SEM images, comprises three characteristic features: shallow ring cracks on the YSZ surface within and up to the contact circle; segments of “cone-like” cracks within the YSZ layer; and delamination at the YSZ/substrate interface with a size less than, or equal to, that of the contact circle. The ring cracks probably form on loading with successively larger radii as the load is increased leading to several concentric cracks within the final contact circle. Such cracks require a tensile radial stress of sufficient magnitude being created near the edge of the contact circle during loading. The cone-like cracks are probably also generated during loading, but open up during unloading when much of the compressive indentation stress relaxes. The interface delamination most likely occurs during unloading as the YSZ tends to relax elastically more than the substrate, which has suffered more plastic deformation due to collapse of the porous structure under the compressive loading stresses.

Table 2 summarises the threshold conditions observed for formation of the first surface ring crack. The threshold load and displacement are the experimentally observed values. The contact radius at the threshold load was obtained from the FE simulations and combined with the experimental peak load to give the threshold mean indentation pressure. This is similar to, but not the same as, the apparent indentation hardness obtained above using the Oliver and Pharr analysis because in the latter case the contact area is estimated from the unloading curve. It is interesting to note from Table 2 that the threshold displacement is almost the same for both oxidised and reduced specimens.

Table 2 Mean pressure at threshold loads for first surface ring crack formation

| Specimen | Threshold load $P$ (mN) | Threshold displacement (nm) | Contact radius deduced from FEM $a$ ( $\mu\text{m}$ ) | Threshold indentation pressure (GPa) |
|----------|-------------------------|-----------------------------|-------------------------------------------------------|--------------------------------------|
| Oxidised | 1900                    | 1811                        | 8.45                                                  | 8.47                                 |
| Reduced  | 1300                    | 1870                        | 7.78                                                  | 6.84                                 |

Examples of the maximum principal stress distributions computed in the FE simulations are shown in Fig. 11.

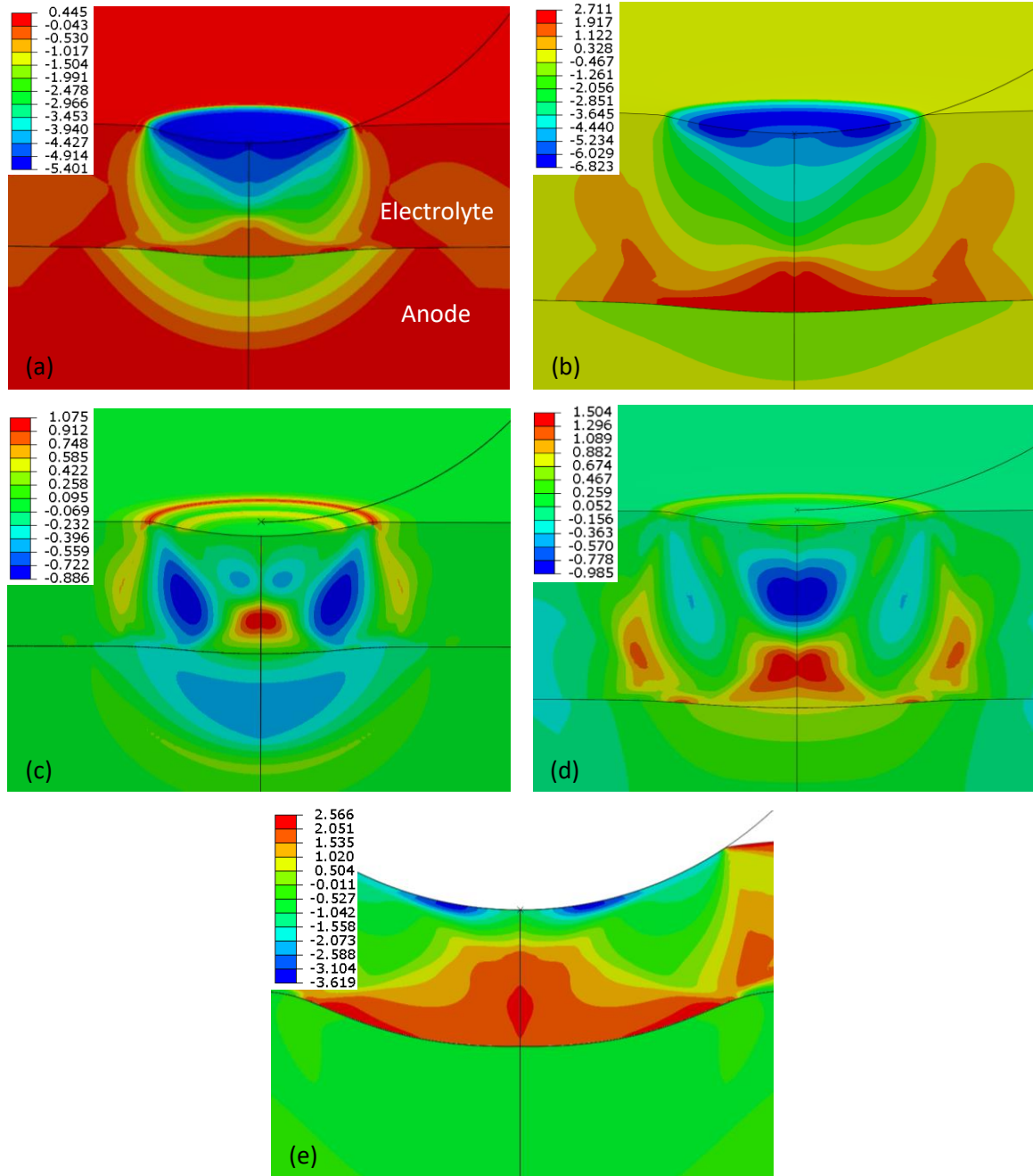


Fig. 11 Maximum principal stress distributions in GPa computed in the FE simulations; (a) at the threshold load of 1900 mN, and (c) after unloading from the threshold loads for the oxidised specimen. (b) At the threshold load of 1300 mN, and (d) after unloading from the threshold load for the reduced specimen. (e) At a peak load of 7000 mN for the oxidised specimen corresponding to the SEM image in Fig. 2 (c). Note the difference in colour of the zero value in each case.

Crack initiation and propagation in such a complicated multi-axial stress field of tensile, compressive and shear stresses is difficult to predict (see for example [25]). Nevertheless, a commonly used criterion for brittle materials is that cracking initiates in regions where the maximum principal stress is tensile and propagates initially in a direction normal to this stress. The general form of the deformation shown in Fig. 11 is biaxial bending the YSZ layer due to the less stiff substrate and resembles the deformation of a ball-on-ring mechanical test. When the sphere is loaded there is a compressive region in the upper part of the YSZ as in indentation of a bulk material, and a tensile region near the lower surface of the YSZ due to the bending of the YSZ layer (Figs. 11(a) and 11(b)).

The tensile stress at the surface near the edge of the contact circle is very limited in both lateral and vertical extent. On unloading, this region of tensile stress is more evident (Fig. 11 (c) and Fig. 11 (d)) but is still highly localised. This implies that the ring cracks are initially very shallow and remain so even on unloading as seen experimentally. Consequently they do not constitute significant damage to the YSZ at the threshold loads.

The tensile stress near the lower surface of the YSZ when the indenter is loaded, shown in Fig. 11(a) and Fig. 11(b), is much more significant. It suggests that the cone-like cracks seen within the YSZ in Fig. 2 are first nucleated in this region and then travel upwards in the YSZ. Due to the compressive region in the YSZ directly under the indenter, and the high residual in-plane compressive stress in the YSZ, these cracks are not able to propagate directly upwards. It is suggested that they are deflected by the compressive stresses to a shallow angle towards the plane of the YSZ layer to give the cone-like cracks seen in Fig. 2. The compressive residual stress is not relaxed by crack segments (or component of crack propagation direction) parallel to the plane of the electrolyte layer, and is still substantially present in the cracked zones seen in the micrographs after unloading. This stress closes crack segments normal to the plane of the YSZ layer so that only segments at a shallow angle exhibit a visible crack opening displacement as seen in the micrographs.

For a circular penny-shaped crack-like defect in a homogeneous far-field stress in Mode I (opening mode) loading the critical stress required to extend the defect is given by,

$$\sigma_c = K_{Ic} \left( \frac{\pi}{4c} \right)^{\frac{1}{2}} \quad \text{for a defect in the bulk and} \quad (2)$$

$$\sigma_c = K_{Ic} \frac{Y}{M} \left( \frac{1}{\pi c} \right)^{\frac{1}{2}} \quad \text{for a defect at a surface} \quad (3)$$

In these expressions  $K_{Ic}$  is the Mode I critical stress intensity and  $c$  is the radius of a bulk defect or the depth of a surface defect [26].  $M$  and  $Y$  are geometrical factors which for similar tape cast YSZ give the ratio  $Y/M = 1.211/0.795 = 1.52$  [26]. For 8YSZ  $K_{Ic} = 1.61 \text{ MPa m}^{1/2}$  [26], while typical defects seen in Figs. 1 and 2 have a maximum size of approximately  $1 \text{ }\mu\text{m}$ . Thus Eqs. (2) and (3) predict the strength for the YSZ layer as 2.02 GPa for a bulk defect and 1.38 GPa for a surface defect.

From the simulation result in Fig. 11 (b) it is seen that the maximum principal tensile stress for the reduced specimen when loaded at the threshold load of 1300 mN is predicted to be between 1.9 and 2.7 GPa in the region at the bottom of the YSZ under the indenter. This is similar to the critical stress of 2 GPa estimated above and suggests that cone-like cracks would be initiated in this specimen at the threshold load for ring cracking of 1300 mN (Table 2). This is also consistent with the more extensive ring cracking seen after indentation at the higher load of 2000 mN in Fig. 2 (b). The simulated stress field in Fig. 11(a) for the oxidised specimen at its threshold load for ring cracking shows a peak tensile maximum principal stress of less than 0.5 GPa at the lower surface of the YSZ. This is significantly lower than 2 GPa and therefore cone cracks are not expected to form at this load in the oxidised specimen. A simulation was therefore performed for this specimen at a higher load of 7000 mN at which cone cracks were observed experimentally in Fig. 2 (c). The result is presented in Fig. 11 (e) and shows extensive regions of maximum principal tensile stress with values between 1.5 and 2.6 GPa. The formation of cone-like cracks under this indentation load is thus also consistent with a critical stress of 2 GPa.

The simulation results in Figs. 11 (c) and 11 (d) show that a tensile stress develops across the YSZ/substrate interface during unloading. This is responsible for the delamination seen at this interface in the micrographs. The simulations show a larger tensile region for the reduced substrate (Fig. 11 (d)) than for the oxidised substrate (Fig. 11 (c)) which is consistent with the larger difference between elastic relaxation on YSZ and substrate in the reduced specimen. Since the delaminated region is small in the case of the oxidised specimen it is feasible to deduce a critical debonding strength for this interface from the FE simulations. The variation of the maximum principal stress along the interface after unloading is plotted in Fig. 12 and reaches a peak value of 120 MPa on the axis of symmetry under the indenter. This gives an approximate value of 120 MPa for the interfacial strength in this sample. It is more than an order of magnitude lower than the critical stress for fracture of the YSZ because of the porosity in the substrate and the damage done to the YSZ/substrate interface during densification under the indentation. In the case of the reduced specimen a similar estimate cannot be made because the

delamination is much larger and a significant relaxation of the stress will have occurred by extension of the delamination.

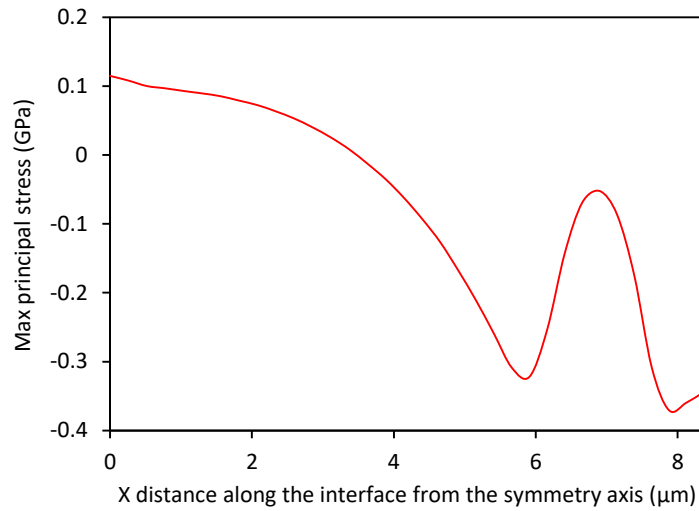


**Fig. 12 Variation in maximum principal stress along the interface between the electrolyte and support computed in the FE simulations after unloading from the threshold load for the oxidised specimen (corresponding to Fig. 11(c)).**

#### IV. Conclusions

Spherical indentation experiments were conducted at loads up to 10 N on bilayer SOFC anode-supported electrolyte (8YSZ) specimens in the as-received (oxidised, NiO-8YSZ composite substrate) and reduced conditions (Ni-8YSZ composite substrate). The YSZ layers were approximately 10 μm thick and the substrates approximately 500 μm thick. The oxidised substrate had a porosity of 14.6% and the reduced substrate 30.1%. The elastic modulus and uniaxial yield stress for both types of substrates were determined by indentation directly onto the substrates. Indentation of the YSZ side of the bilayers at sufficiently low load (and depth) was not noticeably influenced by the substrates and allowed the elastic modulus and yield stress for the YSZ to be determined as 200 GPa and 3.8 GPa. The elastic moduli of the YSZ and the two types of substrate measured by indentation were in good agreement with values obtained by bulk techniques reported in the literature.

Indentation-induced damage in the specimens before and after reduction was investigated based on SEM observation of the top surface of the electrolyte and cross sections made by FIB machining. The observations revealed a threshold load (and threshold indentation pressure) for the generation of detectable surface ring-crack damage to the YSZ which were 1800 – 2000 mN for the oxidised substrate and 1200 – 1400 mN for the reduced substrate. The lower threshold for damage in the case of the reduced substrate is due to its easier plastic deformation as a result of its greater porosity. At higher loads, damage consisted of concentric ring cracks on the top surface, cone-like cracks in the YSZ and delamination at the YSZ/substrate interface. No radial cracks were seen at any of the loads applied.

FE simulations of the indentation were carried out using the Gurson model to account for densification in the plastic deformation of the porous substrates and mechanical property parameters measured as described above. The residual compressive stress in the YSZ was also included in the simulations. The simulated load versus depth responses were in excellent agreement with the measured ones at loads up to the thresholds for initiating damage. The resulting stress distributions showed that the main damage to the YSZ on loading initiates as cone-like cracks in a tensile region near the interface with the substrate as a result of bending under the indenter. An approximate analysis of the failure from defects (residual pores) of size 1 μm seen in the YSZ predicts a failure stress of approximately 2 GPa in acceptable agreement with the simulated stress distributions and experimental observations. The cracks initiated near the YSZ/substrate interface travel towards the top surface of the YSZ, but are deflected towards the horizontal by the compressive indentation and residual stresses. Delamination occurs on unloading due to the elastic recovery of the YSZ being greater than that of the substrates. The

simulations suggest that the stress required to debond the YSZ/oxidised substrate interface is approximately 120 MPa.

The simulations indicate that the residual compressive stress in the YSZ has only a small effect on the apparent elastic modulus of the YSZ and a slightly larger effect on its apparent hardness. However, the experiments suggest that the residual compressive stress has a significant effect on cracking in the YSZ and in particular inhibits crack opening displacements normal to the plane of the YSZ layer. This is important for application in SOFCs as it prevents leakage of fuel across the electrolyte if the electrolyte is damaged.

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### Appendix A. Supplementary data

Raw data on which this paper is based can be openly accessed at <https://dx.doi.org/10.6084/m9.figshare.3317353.v1>

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