COMPARISON OF STRESS GENERATING MECHANISMS
IN A PLANAR SOLID OXIDE FUEL CELL STACK

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ABSTRACT

An understanding of the significance of the mechanical stresses within the fuel cell stack is required to design a fuel cell which will not exhibit poor performance or reduced lifetime. This paper gives a summary of the mechanisms responsible for generating stresses in the planar SOFC and details of attempts which have been made to quantify these stresses. Fail-safe diagrams for informing design choices are discussed.

INTRODUCTION

For a Solid Oxide Fuel Cell (SOFC) to be successful in a commercial environment, consistent performance and long lifetime will be key factors. In the fuel cells built to date, electrochemical performance has been of primary concern and mechanical performance of only secondary importance. However, consistent performance and prolonged lifetime will require mechanical integrity of the SOFC since its lack will lead to detrimental electrical performance and even catastrophic failure. The planar SOFC is now reaching the stage where design scale-up towards commercial sizes is being considered. For these larger stacks mechanical behaviour, and its interaction with electrical performance, becomes increasingly important. This heightened interest in the mechanical performance of fuel cell stacks has been noted in the literature (1, 2).

The aim of this paper is to assess the significance of the stress generating mechanisms in the stack of a planar Solid Oxide Fuel Cell. The mechanisms identified here include thermal expansion mismatch, both within the stack and leading to residual stresses within the stack, temperature gradients across the stack, both steady state and transient, and variations in oxygen partial pressure. The effects due to each are discussed, and their relative importance determined.

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THERMAL EXPANSION MISMATCH

The stringent electrochemical requirements for fuel cell materials make it impossible to select materials which have well matched Coefficients of Thermal Expansion (CTE). The SOFC is subjected to large temperature changes during cell manufacture and operation producing large thermal expansion mismatches between the cell components. If this differential expansion cannot be relaxed by allowing compliant joints between components it must be accommodated by elastic or creep strains within the components.

The stack must be sealed at its edges to prevent the air and fuel flows mixing. Any thermal expansion mismatch between the stack and the mountings used to support it can produce stresses within the cell components. The severity of this problem depends on the stiffness of the joint between the stack and its mountings. In most self-supported designs the PEN is sealed using a glass which is well above its glass transition temperature under cell operating conditions. The seals will therefore show visco-elastic behaviour at the stack operating temperature and are usually assumed to provide negligible restraint to thermal expansion of the stack. When the stack is cooled below the glass transition temperature the seals become rigid and the thermal expansion mismatch between the stack and its mountings must be accommodated by strains within the bipolar plate, electrolyte and the electrodes. The high melting point of the ceramic stack materials allows little creep so these strains are expected to be predominantly elastic. These elastic strains are residual at room temperature or may result in fracture of the seal or one of the stack components. Attempts to quantify the stresses caused by this process have used simple plate modelling. The stack is simplified to a series of rigidly bonded layers. The entire structure is assumed to undergo a uniform temperature drop and the stresses are calculated using plate theory (eg 3, 4, 5).

In a SOFC stack, where many layers are placed on top of each other, bending is prevented. The stresses which are induced by the differential thermal expansions can be determined by considering a simplified stack comprised of one electrolyte and one bipolar plate. For equilibrium, the stress in the electrolyte, $\sigma_e$, is given by

$$\sigma_e = \frac{h_b E_b}{h_e E_e (1 - \nu_e) + h_b E_b (1 - \nu_b)} \Delta T (\alpha_e - \alpha_b)$$  \[1\]

where $h_e$ and $h_b$ are the thicknesses of the electrolyte and bipolar plate respectively, $E_e$ and $E_b$ the respective Young's moduli, $\nu_e$ and $\nu_b$ the Poisson's ratios, $\alpha_e$ and $\alpha_b$ the CTE's and $\Delta T$ the temperature drop from the stress-free state. A similar formula results for stress in the bipolar plate.

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Equation [1] then predicts a tensile stress in the electrolyte of 52MPa and a compressive stress in the bipolar plate of -5.2MPa. Assessing the significance of the tensile stress in the electrolyte requires some knowledge of the failure behaviour of the PEN. Using the results of biaxial flexure strength tests on electrolyte foils and Weibull statistics, and assuming that an acceptable probability of failure for an individual square electrolyte of side 10cm is $10^{-6}$ it can be shown that the limit on the maximum stress in the electrolyte is approximately 50MPa (6, 7). The tensile stress in the electrolyte, calculated above, is therefore significant.

Equation [1] shows that the tensile stress in the electrolyte can be decreased by reducing the effective temperature drop, by using seals which remain compliant to lower temperatures. Several glass ceramics for fuel cell use have been investigated and glass transition temperatures between 450°C and 650°C reported (8). The calculation above therefore provides an upper limit to the residual stress.

Equation [1] also shows that the stress in the electrolyte can be decreased by reducing the thermal expansion mismatch. Since the 8YSZ electrolyte material cannot be altered this implies a change in the CTE of the bipolar plate. This can be achieved by altering the dopant material or dopant concentration for a LaCrO$_3$ bipolar plate. Figure 1 presents the predicted stresses in each layer as a function of the CTE of the bipolar plate. The stresses in all the layers are sensitive to the CTE of the bipolar plate, particularly the electrolyte. Fracture of PEN structures is reported in test stacks when the thermal expansion mismatch, between the bipolar plate and electrolyte, was greater than $0.7 \times 10^{-6} / \text{K}$ (4).

RESIDUAL STRESSES IN THE ELECTRODE/ELECTROLYTE STRUCTURE AFTER MANUFACTURE

The most common method of manufacturing planar self-supported electrode/electrolyte structures is to deposit electrodes onto a pre-sintered electrolyte and then sinter the electrodes. If the electrode were unrestrained this would result in the electrode shrinking during sintering as the porosity is reduced. However, shrinkage in the plane of the electrode is restrained by contact with the electrolyte, generating tensile stresses in the electrode. A more precise understanding of the introduction of these residual stresses is being developed (9).

The residual stress values in two layer structures can also be deduced from measuring the curvature and using Equation [2] for mean stress in layer 1, $\sigma_1$,

$$\sigma_1 = \frac{kE_h h_2}{6h_1(h_1 + h_2)(1 - v_2)}$$ [2]
where \( \kappa \) is the measured curvature, \( h_1 \) and \( h_2 \) are the thicknesses in the two layers, \( E_2 \) and \( \nu_2 \) are the Young's modulus and Poisson's ratio in layer 2. In the current study, the greatest stress in typical electrode/cathode samples was found to be 3.8 MPa compressive (insignificant) in the electrolyte and 14 MPa tensile in the electrode (significant) (7).

Manufacture of the anode involves a reduction step after sintering. The porosity of the anode has been reported to increase when it is reduced and this will accommodate some or all of the volume change due to reduction (10). If the volume change is only partially accommodated by a change in porosity the change in volume must be accommodated by deformation of the electrode.

Figure 2 shows the residual stresses predicted in three layers cathode/electrolyte/anode based on a sintering temperature of 1200°C. These results show that a tensile residual stress is expected in the electrodes which of the order of 100MPa. Considering the high sintering temperatures it seems unlikely that the entire cool-down process will be elastic and some creep of the layers might be expected to reduce the residual stresses, and these are being investigated (9). The results are also sensitive to the elastic properties of the porous electrodes which have not been measured but were estimated from empirical formulae.

Electrode/electrolyte structures are now routinely made without reports of cracking during manufacture because the electrode materials have been selected to avoid these problems. Electrode materials with better electrochemical behaviour exist but the thermal expansion coefficients of these materials differ greatly from 8YSZ producing large residual stresses, and cracking is observed, eg. (11, 12). The crack patterns are illustrated in figure 3 and can all be detrimental to the electrical performance of the stack by damaging the in-plane or through-cell conductivity.

A fracture mechanics based approach to determine whether cracks will propagate during manufacture has been developed based on the residual stresses which are induced in the layers of the electrode/electrolyte structure (7). The energy release rate and toughness for various types of cracks are calculated, and using statistical analysis, parameter values (such as difference in CTE, thickness and Young's modulus of the electrode) are generated for which failure probability is reasonable, say \( 10^{-6} \). By judicious choice of the parameter values, the manufactured electrode/electrolyte structure will have probability of failure less than this value. Figure 4 shows an example of prediction of this nature. The figure also shows the range of typical values for current self supported planar designs. Not surprisingly, these lie below all the curves in the "safe" region.

STEADY STATE TEMPERATURE GRADIENTS

The heat transfer within a planar stack is complicated. Heat is generated by the electrochemical reaction and is transferred between stack components by convection,
radiation and conduction. The rate of the cell reaction depends on the concentration of reactant gasses and on temperature. The concentration of reactant gasses varies as they pass through the stack so that the rate of heat generation by the cell reaction also varies through the stack. These processes result in temperature variations across the stack. Changes to the electrical load also influence the cell reaction producing changes in cell temperatures. These temperature gradients generate stresses within the stack.

A large number of computer models have been produced to predict the variation of temperature, gas composition and current density within planar cells (13, 14, 15). These models couple electrochemical modelling of the cell reactions with thermal modelling of heat transfer between the gas flows and solid cell components. However, the authors are aware of only one attempt to assess the significance of these temperature gradients (16).

This latter study predicts the stresses caused by temperature gradients across 10cm by 10cm electrolyte/electrode structures using the Finite Element method (16). The structure was assumed to be rigidly linked to a sealing ledge, and gave maximum principal stresses in the electrolyte of 26 MPa for external reforming and 250 MPa for internal reforming. In the latter case, there is a significant proportion of the electrolyte with maximum principal stress greater than 100 MPa. However, it is unlikely that the seals which connect the ledge to the electrolyte will be rigid at the cell operating temperature, and this work is being extended to include other boundary conditions.

**TRANSIENT TEMPERATURE GRADIENTS**

During start up and shut down and during changes in electrical load on the stack the temperature distribution may change rapidly. One stack model gives some data on the rate at which the cell temperature responds to an instantaneous change in electrical load (15). This predicts that an instantaneous increase in load from 400 to 500 mAcm$^{-2}$ would produce a rate of change of the maximum stack temperature of 8°C/minute. A heating rate of 6°C/minute is frequently used during high temperature testing of fuel cell components which suggests that significant transient stresses caused by changes in load are unlikely if a suitable control system is used. However an emergency shut down or complete loss of load could introduce much more rapid temperature changes.

**VARIATIONS IN OXYGEN PARTIAL PRESSURE**

Many oxides show a variation in composition with oxygen partial pressure, P(O$_2$) and temperature (17). The different components of the SOFC are subjected to very different oxygen partial pressures (18). Cathode materials show changes in composition accompanied by changes in volume and these produce an expansion mismatch with other
stack components. This expansion mismatch is analogous to a thermal expansion mismatch and generates stresses in a similar way.

When used as a bipolar plate, doped LaCrO$_3$ is subjected to a large difference in P(O$_2$) from one side to the other since air flows over one side and fuel flows over the other. Peak stresses have been calculated in the bipolar plate of between 40 and 50MPa due to this effect for a stack operating at 1000°C (5). These are very high and cracking of the bipolar plate during operation has been reported (19). It was suggested, however, that creep of the bipolar plate during this time may allow the stresses to be relieved.

The calculations also predict an overall expansion of the bipolar plate. If the bipolar plate and electrolyte/electrode structure are rigidly fixed together (unlikely but a useful approximation) this results in a tensile stress in the electrolyte of about 175MPa (5). This is unlikely since glass seals are expected to be very compliant at cell operating temperatures. The variation in oxygen vacancy, and hence strain, through the thickness of the bipolar plate also makes it bend. This bending has been reported to damage the seals making it necessary to mechanically compress the stack to hold the bipolar plates flat (4). These problems can be avoided altogether if a metallic or cermet bipolar plate is used.

The cathode material, Sr doped LaMnO$_3$, also experiences variations in oxygen vacancy concentration during cell operation. This results in a linear expansion of about 0.5% compared with the cathode material in equilibrium with air at the electrode surface (18). This expansion is larger than the thermal expansion mismatch between the cathode and the electrolyte and so appears to be very significant. This effect has not been considered in the choice of cathode materials. As yet no reports of cracking caused by this mechanism have been reported in the literature.

MECHANICALLY APPLIED STRESSES

Thin electrode/electrolyte structures are never flat after manufacture. This is partly due to creep strains during sintering and partly due to the presence of residual stresses. Sandwiching the PEN structure between rigid, flat, bipolar plates will flatten these components producing bending stresses and high stresses at contact points. This problem is partly relieved by placing compliant felts between the bipolar plate and PEN. Handling during manufacture may also impose significant stresses and this limits the maximum size of a PEN structure to about 10cm square (2).

LOCALISED STRESSES / EDGE EFFECTS

The design of the planar SOFC requires materials with different elastic properties to be rigidly joined together. This type of joint is well known to produce stress singularities.
which may cause the joint or material near to the joint to crack (20). This type of failure may occur at the joints between the glass seals and PEN where it is sealed to the sealing ledge and could result in failure of the seal or propagation of a crack into the electrolyte. As yet no data are available in the open literature to determine if this is a significant problem.

DISCUSSION

It is clear that in isolation, some of the stress generating mechanisms induce significant stresses in the SOFC stack. However, it is incorrect to base assessment of design and conclusions solely on these mechanisms acting individually. Whereas it is true that, for example, the individual components will not survive manufacture if the residual stresses in the electrolyte/electrode structure are too large, in a real cell, all the effects will be combined, and it is this combined behaviour which must finally be quantified and assessed. The effects may not all be detrimental because it is possible that some stresses will mitigate others. For example, the combination of the residual stress in the electrolyte (compressive) and the point where the induced steady state thermal stress is greatest (tensile) will act to relieve each other.

In order to generate a complete understanding of an operational stack, the combined stresses must be used to predict whether cracks will be induced and propagated. The fracture mechanics approach which has been used to determine whether electrolyte/electrode structures will survive manufacture can be used in an analogous way for survival in operating conditions, including start-up shut-down, power loss, etc (7). Since the method uses predictions for the stresses in each component, it will work in analogous manner for the combined stresses from all the relevant stress generation mechanisms for whichever situation is being considered. The fail safe diagram that results will be very similar to that shown in Figure 4 except that because the stresses will be different from the conditions shown, the axes will have all their values shifted.

Thus it is possible to combine the knowledge of the various stress generating mechanisms, where the contributions of each of these will be intricately linked to each individual design and will need to be determined afresh, to produce a series of fail-safe diagrams for that design. Alternatively, one fail-safe diagram can be drawn with many curves, and by taking the intersection of all the "safe" regions, suitable parameters and material values can be derived to help generate a good design.

CONCLUSIONS

Simple calculations, indicate that thermal expansion mismatch between the stack and its mountings produce significant tensile stresses when cooled from operating temperature. These stresses can be large enough to fracture the electrolyte. The magnitudes of these
stresses are sensitive to the thermal expansion coefficient of the bipolar plate and the compliance of the seals. Thermal modelling of the planar stacks shows that there will be temperature gradients across the cells in the steady state and during changes in cell load.

Residual stresses in the electrolyte/electrode structure after manufacture can be large enough to produce a wide range of different crack patterns. This has prevented the use of high performance electrode materials because their thermal expansion mismatch with the electrolyte is too high. Methods to predict the residual stresses are currently being developed and will be required for accurate assessment of SOFC designs. It is clear from this study that the combined effects of the stress generating mechanisms is significant.

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Figure 1: Stresses in layers of SOFC stack components after (4)

Figure 2: Residual stresses in PEN structure after manufacture after (4)

Figure 3: Crack patterns observed during manufacture of PEN structures

Figure 4: Fail-safe Diagram for 2-layer electrode electrolyte specimen showing sensitivity to the thickness and coefficient of thermal expansion of the electrode