LOW-COST SINGLE-STEP CO-FIRING TECHNIQUE FOR SOFC MANUFACTURING

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ABSTRACT

One-step co-sintering process is the desired low-cost manufacturing process for planar anode-supported solid oxide fuel cell (SOFC) manufacturing. However, a successful one-step co-firing of the multi-layer structure requires that we are able to lower sintering temperature to minimize chemical interaction between the various layers (components) and the distortion of the structure (camber) due to mismatch in thermo-mechanical and physical properties of the individual layers. For the yttria-stabilized zirconia (YSZ) electrolyte material, it was observed that by adding 0.2 mole% nano-sized alumina to submicron-sized YSZ, the relative density increased from 73% to over 93% at a sintering temperature of 1250°C. Initial experimental results indicated that the sintering shrinkage and thickness of the pre-reduced NiO-YSZ anode support are extremely important for controlling the camber (distortion) that develops during the co-firing steps. A detailed finite element model is being developed to guide us in minimizing the experiments needed in selecting the processing parameters required for manufacturing camber-free co-fired cells.

INTRODUCTION

Single step co-firing of electrode and electrolyte layers is a low-cost solid oxide fuel cell (SOFC) manufacturing technique and the successful application of this technique would increase production throughput and decrease energy usage during manufacturing. The multi-layer components of the planar SOFC are fabricated sequentially in the green state by tape-casting and screen-printing techniques and then co-fired at 1300°C as described in the flowchart in Figure 1. However, a successful one-step co-firing of the multi-layer structure requires that we are able to minimize chemical interaction between the various layers (components) and the distortion of the structure (camber) due to mismatch in thermo-mechanical and physical properties of the individual layers. By minimizing the co-firing temperature it is possible to minimize chemical interaction (1,2,3) and in addition by eliminating the temperature gradients within the sample and controlling the shrinkages and dimensions of the individual layers, one can minimize distortion of the structure. The lower bound for the co-firing temperature is dictated by the YSZ electrolyte since it has the highest sintering temperature. The two main challenges of the
one step co-firing process are the densification of the electrolyte and the concave-up cambering of the anode-electrolyte bi-layer structure (Figure 2).

Figure 1. The proposed flowchart of fuel cell manufacturing process.

Figure 2. Two kinds of defects after co-firing; (a) porous electrolyte; (b) camber.

In this paper, the results of research aimed at obtaining a dense electrolyte and camber-free electrolyte/pre-reduced anode bi-layer structure at a co-firing temperature of 1300°C is presented.

MANUFACTURING PROCEDURE

In this work, anode tape casting is accomplished by an in-house tape caster and screen printing of the electrolyte is performed using an EKRA America E1 screen printer. During co-firing, the bi-layer structure is initially heated at 5°C/min rate to 300°C and held at that temperature for two hours for binder removal and then heated at 5°C/min to 1300°C, and held for four hours for sintering. The structure is then cooled at a 5°C/min rate to room temperature.
RESULTS ON YSZ ELECTROLYTE

One of the primary objectives of our investigation was to lower the sintering temperature of the electrolyte. It is known that the final relative density of the electrolyte layer is mainly determined by the screen printing slurry composition and the co-firing temperature profile. Since the target co-firing temperature is 1300°C, the electrolyte slurry composition has is the principal parameter to be optimized.

Pellets were used to explore sintering characteristics of different solids loadings of the electrolyte screen printing slurry with small amounts (<0.5 mole %) of nano-sized γ-Al₂O₃ powder. The pellets were made by uniaxial pressing with a pressure of 5000 psi. In these experiments, submicron-sized YSZ powder, nano-sized YSZ powder and alumina powder were purchased from Tosoh Japan, NexTech Materials, USA and Aldrich, respectively. The particle sizes of submicron-sized YSZ powder and nano-sized YSZ powder were 0.1 μm (analyzed by Horiba 910 Laser Scatter Particle Size Analyzer) and 5 to 10 nm, respectively. The particle size of nano-sized γ-Al₂O₃ powder was 40 nm.

According to Bernard (4), the solubility of Al₂O₃ in YSZ at 1300°C is 0.1 mol%. Therefore, in our experiments, 0.1, 0.2, and 0.5 mol% Al₂O₃ were added to the pellets. Figure 3 shows that for pellets with different mixtures of nano and submicron-sized powders, the relative density reaches a maximum at 0.2 mol% Al₂O₃, and Al₂O₃ has a much greater effect on the sintering of the submicron-sized YSZ powder than on the other powder mixtures. It also shows that without the nano-sized Al₂O₃ powder, the relative density of pellet of pure nano-sized YSZ powder is higher than that of pellets with 50/50 micron-nano sized YSZ mixture or pure submicron-sized YSZ powder. This is likely due to the high surface area of the nano-sized YSZ powders. Further increasing the amount of alumina beyond 0.2 mole% does not appear to increase the relative density.

![Figure 3. Relative densities of different solid loading with addition of nano-sized Al₂O₃ powder after being sintered at 1250°C.](image)

From Figure 3, the highest relative density of 93% was obtained at 1250°C with submicron-sized YSZ powders and 0.2 mole % nano-sized alumina powders.
Figure 4. SEM micrographs of pellets sintered at 1250°C with (a) submicron-sized YSZ powder and (b) submicron-sized YSZ powder and nano-sized Al2O3 powder.

Figure 4 shows the SEM fractographs of the pellets of submicron-sized YSZ powder. It shows that after sintering, without nano-sized alumina, the pellet is still porous (73% dense), and when nano-sized alumina powder is added, it improves the sintering characteristics and the porosity decreases significantly (93% dense); no connected porosity is seen.

The screen printed electrolyte layer with the optimized slurry composition produces a higher relative density with no connected pores. Figure 5 shows such a dense electrolyte layer after being co-fired with the pre-reduced anode layer at 1300°C.

Figure 5. A dense electrolyte layer one pre-reduced anode after being co-fired at 1300°C.

NEED FOR CAMBER REDUCTION

After the parameters were optimized for the electrolyte screen printing process, a dense electrolyte layer was obtained after sintering at 1300°C, but a camber still existed in the
anode-electrolyte bi-layer structure. Because of the high non-linearity of the camber formation, a finite element model was developed to simulate the co-firing process. The simulation results provided insight into the effect of various process parameters on camber formation process. The information was used to optimize the process parameters in order to eliminate the camber.

THERMO-MECHANICAL MODELING OF THE CO-FIRING PROCESS

Constitutive Equations

In the co-firing process, the materials show different behavior at different temperature ranges, so the co-firing process is divided into two material regimes, one is the thermo-elastic regime, where material elasticity and thermal expansion are considered, and the other regime is thermo-visco-elastic regime, where viscosity is considered, besides elasticity and thermal expansion mentioned above. In the simulation we assume that for both YSZ electrolyte and NiO+YSZ layer, when temperature is above 800°C, the materials enter thermal-visco-elastic regime. Because the cathode is thin and very porous before and after sintering, only YSZ electrolyte layer and NiO+YSZ layer (anode layer before reduction) were considered in the model.

In the thermo-elastic regime, the mechanical constitutive equations can be expressed as:

$$\sigma_{ij} = C_{ijkl} \epsilon_{ijkl}^\text{total} + \alpha \Delta T \delta_{ij}$$  \[1\]

Where $\sigma_{ij}$ is the stress tensor, $C_{ijkl}$ is the material stiffness tensor, which is a function of temperature $T$ and relative density $\rho_r$. $\epsilon_{ijkl}^\text{total}$ is the total strain tensor, $\alpha$ is the thermal expansion coefficient (CTE), and $\delta_{ij}$ is the Kronecker delta.

In the thermo-visco-elastic regime, according to Bordia (5), Gillia (6) and Du (7) the total strain tensor during sintering comprises elastic, thermal and visco-plastic components. Following Bordia (5) and Gillia (6) it can be shown that the strain rate is given by,

$$\dot{\sigma}_{ij} = C_{ijkl} \epsilon_{ijkl}^\text{total} + \alpha \Delta T \delta_{ij} - \left( \frac{\sigma_{mm} - P_L}{2G} \right) \frac{\delta_{ij}}{3K}$$  \[2\]

where $\dot{\sigma}_{ij}$ is the stress rate tensor, $\Delta T$ is the rate of change of temperature, $\sigma_{ij}' = \sigma_{ij} - \frac{\sigma_{kk}}{3} \delta_{ij}$ is the deviatoric stress tensor, $P_L$ is the sintering stress, $G$ is the effective shear viscosity, and $k$ is the effective bulk viscosity. $P_L$, $G$, and $K$ are functions of temperature and relative density of the material, and according to Skorohod (8) and Olevsky (9):

$$G = \eta_b \rho_r^2$$  \[3\]

$$K = \frac{2}{3} \eta_b \rho_r^3$$  \[4\]

$$P_L = \frac{3\sigma}{r} \rho_r^2$$  \[5\]
where \( \eta_0 \) is the material uniaxial viscosity, \( \sigma \) is surface tension and \( r \) is the particle size of the sintering material.

Based on energy balance, the thermal constitutive equations in both regimes can be expressed as

\[
\rho(T, \rho_r) \cdot c_p(T) \cdot \frac{\partial T}{\partial t} = k(T, \rho_r) \cdot \nabla^2 T
\]

where \( \rho \) and \( k \) are material density and thermal conductivity, respectively. They are functions of temperature and material relative density, \( C_p \) is the specific heat, a function of temperature.

Table 1 lists part of the material property values used in the simulation model for nominal condition.

| Property                      | Anode     | Electrolyte |
|-------------------------------|-----------|-------------|
| Density* (kg/m³)              | 6430(10)  | 6000(11)    |
| Young’s modulus* (GPa)        | 218.8(10) | 220.8(12,13,14) |
| Poisson’s ratio*              | 0.358(10) | 0.316 (12,13,14) |
| CTE (10⁻⁵/K)                  | 13.4(15)  | 10.8 (16)   |
| Thermal conductivity* (W/(m.K)) | 19 (17)   | 1.85 (18)   |
| Specific heat (J/kg)          | 459.9+0.087T(17) | -61.028+2627T(11) |
| Initial relative density      | 0.55      | 0.65        |
| Uniaxial viscosity* (GPa.s)   | \(10^6\) (assumed) (19) | \(10^6\) (assumed) (19) |
| Particle diameter (µm)        | 1         | 0.1         |

*fully dense material property

The commercial available finite element code ABAQUS was used to run the simulation, and the constitutive equations were applied in the user-defined function UMAT and UMATHT. The simulations were run on a Pentium V 2.8GHz PC with 1GB memory.

Simulation Results and Analysis

Figure 6 shows the camber changes with time according to the model at nominal condition. It shows the camber formation is mainly in the thermo-visco-elastic regime (sintering period), and the camber magnitude increases, reaches a maximum and then decreases. Figure 6 also shows that the hydrostatic pressures \( P \) in the anode and electrolyte layers reach a maximum, then decrease, following the same trends as the camber. \( P \) is defined as \( P = -\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \), negative \( P \) is tension and positive \( P \) is compression; thus Figure 6 also shows that the electrolyte layer is in tension and the anode layer is in compression.
Figure 6. Camber magnitude and pressure change with time during co-firing.

Parametric Studies

Figure 7. Parametric study of the anode.

Figure 7(a) shows that when the linear shrinkage of the anode increases, the magnitude of the negative camber decreases and when it is larger than that of the electrolyte layer (13.2% by simulation on single layer), positive camber occurs. Figure 7(b) shows the camber changes with time for the anode/electrolyte bi-layer structure as a function of anode thickness. It shows that as anode thickness increases, the camber decreases. In summary, the finite element simulation results show that matching the shrinkages of anode and electrolyte layers decreases the camber greatly, and increasing anode thickness can also decrease magnitude of the camber.

RESULTS ON ANODE

The research on the anode mainly focused on improving its linear shrinkage and increasing its thickness to reduce camber. When the sintering temperature profile is fixed, the linear shrinkage depends on the slurry composition, so anode slurry composition was optimized to match shrinkage with that of the electrolyte. The anode layer thickness was increased by laminating multiple anode layers. In the anode slurry, Hypermer™ KD4 was the dispersant, ethanol and toluene were the solvents, PVB was the binder, and Santizer™ 160 was the plasticizer. Experimental results show that the tape shrinkage can
be increased by decreasing total volume percentage of the dispersant, binder and plasticizer. When the anode tapes were sintered under the same temperature profile as the co-firing process, the results are shown in figure 8.

![Figure 8](image)

**Figure 8.** Linear shrinkage decreases with increasing total volume percentage of dispersant, binder and plasticizer.

The reason for increased anode-tape shrinkage with less total volume percentage of dispersant, binder and plasticizer is likely due to the higher pre-sintering green density. When the sample has higher pre-sintering green density, during sintering, the sintering stress is higher according to equation 5, and thus exhibits larger shrinkage.

**CONCLUSIONS**

One-step co-sintering process is the desired low-cost manufacturing process for planar anode-supported solid oxide fuel cell manufacturing. Electrolyte layer densification and camber are two challenges to the successful application of the technique. Our work shows that by adding 0.2 mol% of nano-sized alumina powder to sub-micron size YSZ powder, the relative density can be increased from 73% to over 93% at a sintering temperature of 1250°C. Further, increasing anode tape shrinkage and thickness reduces camber. A detailed finite element model is being developed to guide us in minimizing the experiments needed for selecting the processing parameters required for manufacturing camber-free co-fired solid oxide fuel cells. Through the experimental and modeling efforts, dense, flat electrolyte-anode bi-layer structure was obtained by co-firing the structure at 1300°C.

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