FABRICATION OF AN ANODE SUPPORTED TUBULAR SOFC SYSTEM

Nigel Sammes and Yanhai Du
Mechanical Engineering Department, University of Connecticut
44 Weaver Rd, Unit 5233, Storrs, CT 06269-5233, USA

ABSTRACT

Tubular SOFC systems have many desirable characteristics compared to their planar counterparts, however there are many obstacles and difficulties that must be met to achieve a successful and economically viable manufacturing process and stack design. Anode supported tubes provide an excellent platform for individual cells. They allow for a thin electrolyte layer, which helps to minimize polarization losses, to be applied to the outside of the tube, thus avoiding the difficulty of coating the inside of an electrolyte or cathode supported tube, or the stack design problem of having a fuel chamber if the anode is on the outside of the tube. This paper describes the fabrication of a traditional (Ni-YSZ) anode tube via extrusion of a plastic mass through a die of the required dimensions. The anode tubes were dried before firing, and tests performed on the tubes to determine the effects of pre-firing temperature on porosity. The porous tubes had a vacuum applied to the inside while being submerged in aqueous electrolyte slurry. Various parameters were examined, including vacuum pressure, submergence time, and drying conditions, and studied using light microscopy. Cathode coatings were applied using a brush painting technique, and optimized as a function of paint consistency, drying conditions, and firing temperatures.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are a promising candidate for many power generation schemes from small systems of a few watts up to megawatt-sized power plants. They have a high thermodynamic efficiency and can operate on many different fuels. The two major stack designs can be classified as planar and tubular. Tubular systems have many fabrication advantages, which is paid for by a reduction in total stack performance. This is due to the geometry of the stack, which does not contain as much effective cell area in a given volume as a planar stack. In cases where total stack volume is not an issue, tubular stacks have many advantages. Planar systems require gas sealing between each cell and around all edges and manifolds, each of these areas are at the cell’s operating temperature [1-2]. Tubular stacks only require sealing where the manifolds connect to the cells; this area can be kept outside of the active cell zone where temperatures will be lower. Utilizing anode support also has many benefits both for fabrication and performance. An anode support tube allows a thin-coated electrolyte to be placed on the supporting anode, which reduces electrolytic resistance losses and yields better conductance at lower temperatures. Anode materials, such as Ni-YSZ, are less expensive
than the traditional (expensive) lanthanum manganite (LSM) materials used in cathode support tubes; making an anode support lowers the overall amount of LSM used and lowers total stack cost. Another benefit of anode support over cathode support is the fuel/oxidant arrangement. For anode support with electrolyte and cathode layers on the outside, fuel is passed through the tube and ambient air on the outside.

For this project, nickel yttria stabilized zirconia (Ni-YSZ) cermet anode supported tubes with a thin coat YSZ electrolyte and a thin coat lanthanum strontium magnete cathode. The goal of this study was to optimize fabrication techniques for these tubular cells [3-6].

**EXPERIMENTAL**

Ni-YSZ tubes were extruded from a plastic mass through a die. The mass was synthesized by mixing commercially available nickel oxide with 8 mol% YSZ (Tosoh) powder, (traditionally 50% nickel oxide and 50% 8YSZ by mass), with a commercial plasticizer, methylcellulose. This was mixed with DI water for several hours and left to age overnight. A vacuum was applied to the mixing chamber for a short period to remove air bubbles from the mass. The mass was extruded using a commercial extruder (15 ton Jaygo), with an in-house designed die. The extruded tubes were dried in Teflon holders to minimize bending. The dried tubes where then cut to length. These tubes were pre-fired to various temperatures in an alumina shell to keep the anode tubes straight. The pre-fired tubes were dipped into an 8YSZ (Tosoh) aqueous slurry with a vacuum drawn on the inside. Pre-fire temperature, vacuum pressure, and submersion time were varied to determine the best conditions for a crack-free coating. A pump was used to circulate the slurry to keep it well mixed. The coatings were left to dry in air, then placed in an oven at approximately 50°C. After drying the tubes were placed onto an YSZ coated alumina shell with YSZ coated alumina tubes to prevent bending, and fired to 1450°C (see later for reason). Light microscopy was used to determine the presence of cracks.

A second coating method was used for comparison. An 8YSZ paint was made by diluting a commercially available non-aqueous ink with ethanol 2:1 by mass. This paint was applied using a brush coating technique where the tube is turned on a lathe and the paint is applied to the turning tube with a brush. These coatings were left to dry overnight and fired using the same method as the slurry coatings. To test the coating for gas tightness the anode must be reduced. A quartz reduction chamber was used to contain a reducing atmosphere while being heated to 800°C. Nitrogen was used to purge up to 200°C, then hydrogen was passed through the chamber at approximately 0.5 L/min until the temperature returned to 200°C on cool down, when nitrogen was purged until room temperature. The now porous tubes allowed for testing of the YSZ coating. Two methods were used to test the tubes. A vacuum was applied to the inside of the tube and the time it took to go from 20 in Hg to 10 in Hg was measured. The tubes were also pressurized with nitrogen and submerged in water; bubbles would form if cracks, pinholes or porosity were present in the tube.

The cathode was applied using a brush painting technique similar to the second electrolyte coating method. The paint was made from commercially available LSM ink by diluting with ethanol 2:1 by mass. The paint was applied; again, by turning the tube
on a lathe and painting with an artist's brush, approximately 19 mm was left uncoated at each end. The cathode was fired to 1100°C with tubes supported by the uncoated end to prevent damage to the cathode.

The cathode current collector was made from silver wire and a silver wire braid. Several flat braids of silver wire 0.125" wide were laid along the length of the tube, while silver wire was wrapped around the circumference. The circumferential wire and silver paste serve both to improve the electrical connection and the mechanically attach the current collector, while the flat braid acts as a bus to reduce the length of wire the current has to travel.

RESULTS AND DISCUSSION

Figure 1 shows a plot of firing shrinkage as a function of firing temperature for the anode tubes. Above 1300°C, little further shrinkage was observed; thus the tubes were typically sintered at between 1300°C and 1450°C.

![Figure 1. Firing shrinkage as a function of firing temperature.](image1)

![Figure 2. Effect of firing temperature on anode density and porosity.](image2)
Figure 2 shows the correlation between the firing temperature and the density/porosity of the anode tubes. The materials were increasing in density as the firing temperature approached 1400°C while the porosity significantly decreased to below 5%. The porosity, however, recovered approximately 20% from reducing the anode (NiO to Ni).

The electrical resistances of the reduced tubes were measured using standard DC techniques and were found to be less than 0.05 Ωcm$^{-1}$ for all tubes produced.

The major obstacle in creating a crack free coating is thickness. If the coating is applied too thick, it cracks as shown in Figure 3.

![Figure 3. Mud cracking due to excess coating thickness.](image)

Multiple dips were tried to even-out coats and build thickness without cracking. However, since the first coating filled the pores, the vacuum no longer had an effect, and the subsequent coats were thinner and did not adhere well to the tube. Runs and drips formed causing thick areas, which cracked during drying. A crack formation time line was made to determine when cracks were formed. If cracks formed, they did so during the first few hours of drying and grew throughout the drying process. However, they did not form during firing. Figure 4 shows a series of micrographs of the same tube during various points on this time line. Tube A shows cracks formed during the overnight drying which become more defined after sintering, although no more are produced. Sample B has no cracks at any point during drying, and thus no cracks are formed after firing.

(a): Tube A dried overnight  
(b): Tube A sintered 1450°C
When the tubes were pressurized and submerged in water it was apparent that under certain coating conditions, a significant amount of leakage occurred at the interface of the tubing and tube, as well, as a smaller percentage of leakage through the wall of the tube; Figure 5 shows a photograph of a failed sample.

Optimization of the 8YSZ coating was realized when the correct firing regime, reduction regime and coating thickness were applied (see reference 7 for details).

Microscopy also showed a difference in microstructure. The slurry coatings had a very small honeycomb pattern when magnified 1000x however the paint coatings showed a tight agglomerate structure. Figure 6 shows a cross-section of a well adhered, pin-hole free Ni/8YSZ tube coated with 8YSZ electrolyte, while Figure 7 shows a photograph of the 8YSZ coated anode support tube.

The cathode (LSM) coatings were all well adhered and could not be removed by scratching or with adhesive tape (see Figure 8 for SEM micrographs of the deposited cathode). Figure 9 shows the single fuel cells fabricated under the optimized conditions. Cell performance is currently being performed, and will be reported elsewhere.
Figure 6. SEM micrographs of the cross-section of a pin-hole free Ni/8YSZ tube coated with 8YSZ electrolyte.

Figure 7. Photograph of a 8YSZ coated anode support tube (15 inches long).

Figure 8. (a) SEM of sintered cathode and (b) the image object process result.

Figure 9. Anode supported tubular single fuel cells.
Results from some provisional tests on the cell described above are shown in Figure 10. For the optimized cells, run on hydrogen/3% steam, a power output of ~ 650 mW/cm² could be realized. Long term testing and redox behavior is now being studied, and will be reported elsewhere. However, it is quite apparent that the results are encouraging.

CONCLUSIONS

Anode supported tubes provide an excellent platform for SOFC fabrication. They possess high-energy conversion efficiency as well as a geometry with many desirable properties. Tube extrusion can be done very rapidly and easily. After the tubes are dried and fully sintered, a dense YSZ coating can be applied using a simple brush painting technique. A similar technique can be used to apply an LSM coat. These tubes can be assembled in stacks and operated at a range of temperatures on several different fuels to produce clean power. The next part of this work will be to electrically test the SOFC tubes in single and small stack configurations.

REFERENCES

1. J. Larminie, A. Dicks, Fuel Cell Systems Explained, John Wiley & Sons Ltd., (2000).
2. G. DiGiuseppe, J. R. Selman, J. of Materials Research, 16(10), 2983-91 (2001).
3. Y. Du, N. M. Sammes, Solid State Ionics, 9, 7-14 (2003).
4. Y. Du, N. M. Sammes, J. of European Ceramic Society, 20, 959-965 (2000).
5. Y. Du, N. M. Sammes, J. of European Ceramic Society, 21, 727-735 (2000).
6. Y. Du, N. M. Sammes, et al., J. of Electrochemical Society, 150, A74-A78 (2003).
7. N. M. Sammes, Y. Du and R. England, US Patent Application, UCT-0042, (2003).