LOW COST SOLID OXIDE FUEL CELL STACK DESIGN USING EXTRUDED HONEYCOMB TECHNOLOGY

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ABSTRACT

Cost has become a critical issue in the maturing technology of solid oxide fuel cells (SOFCs). While many seek new materials to improve cell performance, there comes a realization that the economics of fabricating a functional stack may drive commercialization faster than any performance issue.

To this end, a novel fabrication technique is described which allows the simultaneous fabrication of both electrolytes and interconnects in a single hermetic package. Two key issues in this design involve the fabrication of honeycomb structures and the reduction of metal oxides during the sintering process to develop integral interconnects. The result is a highly scalable and cost effective method to produce SOFC stacks.

INTRODUCTION

Solid oxide fuel cells (SOFCs) represent one of the most efficient means of converting chemical energy to electricity. The challenges facing SOFC technology is cost reduction and economic competitiveness. While many laboratories have demonstrated remarkable single cell performance (1-5), the current difficulties lie in the construction of substantial stacks. Structural issues and sealing issues inherent in joining dissimilar materials continue to plague a young and emerging industry. Much of this is evolved from a mindset of trying to join functional single cells to produce a stack of cells rather than producing a stack from the onset.

From the standpoint of both the planar and the tubular designs focused on today, each has evolved from a single cell and the concept of producing a stack has been an afterthought. The tubular design is inherently advantageous since the tube offers the possibility of creating gas seals outside of the functional high temperature zone (6). Planar stacks have the advantage of high power densities (7). Honeycomb stack design offers the energy density of planar stacks with the possibility of cold gas seals from tubular design.

The honeycomb approach utilizes the same extrusion technology from which automobile catalytic converters are produced. In this communication, we report the concept and conceptual design of honeycomb type fuel cell stacks and our initial results on the fabrication of fuel cell stacks using extrusion.
The purpose of this design is to provide a cost effective method for the production of SOFCs. The specifics of the design dictate the eventual outcome of this effort. Two unique variations have come from these design efforts, which we call the monolithic and hybrid designs. In the monolithic design, the extrusion is made completely from electrolyte, whereas the hybrid design uses the layered approach to create a stack. Each design has specific advantages, which can be exploited for particular applications.

**Monolithic Design**

The advantage of the monolithic design is its simplicity. The extrusion of a single material can be achieved effortlessly, as is done on a regular basis in the catalyst support industry. Firing is achieved in air, without the complications of differential shrinkage. The major drawback is that without the interconnect layers, the current must be drawn through the thin section of the electrode for the length of the cell. The device essentially ends up as a single cell, which is folded back and forth across itself. Without substantial external wiring, the device delivers less than 1 volt at very high current.

Since each layer of the device is actively generating power, there is a potential for very high power densities. However, as the device is scaled-up, the power, which must pass through the electrode, will become too high, and lead to substantial ohmic losses. Filling the channels with a porous current collector will mediate this effect to some extent but this design is ideally suited to small power applications (less than 50W), particularly where high power density is an issue.

**Hybrid Design**

The hybrid design, incorporating alternating layers of electrolyte and current collector, is not limited by the amount of current passing through the cell. The current is drawn vertically through the cell, using the stack design to develop voltage rather than current. Adjusting the height of the cell (number of stacked layers) versus the length of the extrusion will allow a design for the desired power at a specified voltage. The hybrid design sacrifices some of the power density of the monolithic design by replacing active electrolyte (the source of power) with interconnect material.

Complications in the fabrication of the hybrid structure are its major drawback. The issues include the co-extrusion of layers simultaneously, matched drying shrinkage, control of firing shrinkage, and adhesion of the dissimilar materials. Once it is fabricated, issues of differential thermal expansion and interconnect corrosion will become critical.

Square cellular extrusions are the base for the overall design. Simultaneous extrusion of alternating layers of electrolyte and interconnect precursor pastes (hybrid design) allows for the production of a stack in a single extrusion process. Figure 1 shows a conceptual drawing of the hybrid extruded honeycomb cell. From a cost perspective, this is a tremendous saving over creating individual cells and creating a stack from these elements. It is akin to the change from the production and assembly of individual electronic components on circuit boards to the mass production of integrated circuits whereby many thousands of components are fabricated simultaneously.
Of the four essential layers of a fuel cell (interconnect, anode, electrolyte, and cathode) the two chosen for extrusion are the ones that are required to be dense and hermetic. This is critical, since they serve as the structural backbone of the stack. Anode and cathode materials fill the open channels and serve no structural purpose, which is best since they are porous and not suited as structural members. The open cell design also offers high compliance allowing the relaxation of the inevitable thermal stresses evolved within the structure upon cycling. Further, the metallic portion can be tailored to have a yield point below that of the electrolyte, causing it to plastically deform rather than allow failure of the ceramic.

**Expected Power**

The low cost of fabrication is accentuated by the anticipated performance from such a stack design. Single cell data and measurements made using extruded electrolyte have been combined in models to predict the performance of monolithic and hybrid cells fabricated using this technique. From these models, the values for our current process (300 μm YSZ) and our anticipated end goal (30 μm Sc₂Zr₂O₇) have been evaluated for power density and specific power. This data is summarized below in Table 1.

State of the art honeycomb fuel cells may encompass many new ideas too numerous to list out completely. A few of these include the use of thinner extrusions (30 μm is currently state of the art), ceria based electrolytes, and advanced electrode materials. Taking these possibilities into account, achievements such as power densities over 5 W/cc, operating temperatures nearing 400°C, and costs in the range of $50 /kW seem possible in the near future using this technology.

**Table 1. Predicted Performance of Various Honeycomb Fuel Cells.**

| Design   | Current | Near Future | Future |
|----------|---------|-------------|--------|
|          | Monolithic* | Hybrid¹ | Monolithic* | Hybrid¹ | Hybrid¹ |
| Electrolyte | YSZ | YSZ | ScSZ | ScSZ | Ceria |
| Thickness (microns) | 300 | 300 | 60 | 60 | 30 |
| Temperature (C) | 700 | 700 | 700 | 700 | 500 |
| Power Density (W/cc) | 0.388 | 0.205 | 7.29 | 4.48 | 9.27 |
| Specific Power (W/g) | 0.086 | 0.034 | 1.67 | 0.91 | 1.37 |

* Calculated for 20 Watt cell
¹ Calculated for 100 Watts delivered at 12 Volts

After the extrusion is complete, but before firing, alternating layers are plugged on opposite ends of the extrusion. This allows fuel or air to be easily supplied to the appropriate layers of the stack. Exhaust holes are drilled through the side of the extrusion at the opposite end of the gas channels to allow the gas to pass through the stack (Figure 2). After an initial firing, the electrode materials are flow coated through the open channels in the same manner that the gas will flow through during operation.

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EXPERIMENTAL

Initial extrusions have been produced solely from yttria stabilized zirconia (YSZ) electrolyte for the purpose of fine tuning the extrusion and firing processes. The YSZ powders are from a commercial supplier and are produced into a 150 gm batch of paste using a Haake rheometer, which has a paste-compounding chamber. The pastes produced have yield strength in the range of 400 to 500 kPa as measured by capillary rheometer. Similar pastes are produced using transition metal oxide (TMO) precursors for the interconnect portion of the extrusion.

Extrusion dies, originally made from aluminum, are now produced from 17-4 stainless steel. Dies have been made to extrude progressively thinner wall dimensions, beginning at 375 µm and are currently at 180 µm. As the wall dimensions shrink, the cell size also shrinks, yielding a constant 15% total density for the extrusion. The pastes are initially extruded into 10mm diameter rods to use as feedstock for the square cell extruder. For our 4 x 4 cell extrusion, a feed barrel has been produced which feed each of the five layers of the structure with its own feedstock. In the case of pure electrolyte, the feedstock is composed of 5 rods of zirconia electrolyte paste. For the Hybrid structure, the top, bottom and middle rows are replaced with TMO paste.

The extruder is positioned vertically, allowing about 20 cm of paste to be extruded. The extrusion is allowed to dry suspended in this vertical position for several minutes before handling. Final drying occurs over several days in a controlled environment. Once dry, the extrusions are easily handled. This allows them to be cut to length and modified for gas manifolding. The initial firing takes place after the manifolding is complete. A firing cycle was developed using a non-contact dilatometer. The goal is to use both temperature and atmosphere to control the shrinkage of both phases simultaneously.

Electrode powders are produced by either solid-state or glycine nitrate process. Phase identification is performed using x-ray diffraction (Phillips PW-1800). Powders are combined with acetone and an organic binder to produce slurries of appropriate viscosity for flow coating of electrode powders through the gas channels. Multiple layers of electrode slurries are applied to achieve the desired electrode thickness and layering of materials to optimize properties. Firing appropriate to each anode and cathode are performed in order of decreasing temperature.

RESULTS

Extrusion

Initial extrusions of YSZ electrolyte alone were produced to define the process for electroding and manifolding. The initial die had wall thickness of 375 µm, and YSZ electrolyte samples extruded through this die were fired at 1400°C. This yielded a wall density of 5.65 g/cc and a fired thickness of 280 µm. Figure 3 shows these first fired samples along with early efforts at gas porting. This extrusion was achieved using an aluminum die like that pictured in Figure 4. Many initial extrusions were used to develop the coating procedure for applying electrodes.
To produce layered structures, a new die, which allowed separate feedstock to each layer, was required. The new die design is seen in Figure 5. This die allows the insertion of 5 separate pastes to create 5 layers of the extrusion. The pastes used must match in their yield strengths (bulk yield stress and die wall shear stress) in order to extrude at similar rates. Figure 6 shows a hybrid extrusion composed of YSZ and Inconel 617 alloy (In617). The unfired extrusion has wall thickness of 180 μm and shows little curvature over a 17 cm length. Joints between the electrolyte and interconnect paste seem well knitted and uniformly centered between within each cell layer.

**Firing**

Substantial work has been performed using an automated non-contact dilatometer to understand the sintering process for all of the potential materials involved. Shrinkage of the various components comes primarily from binder bum-off, oxide reduction, and sintering densification. These studies indicate that the shrinkage occurs over a vastly different temperature regime at a different rate for electrolyte and interconnect materials. Inconel 617 was chosen as one of the candidate interconnect materials for all work based on data indicating a close match of thermal expansion to that of zirconia based electrolytes and the viability of Fe-Cr ferritic steels. This process also hinges around the premise that for alloys processed via direct reduction of TMO paste, the total amount of shrinkage encountered is similar to that of YSZ after sintering.

Typically during the fabrication of metal parts using direct reduction of TMO materials, the material is fired in a highly reducing atmosphere. Shrinkage occurs initially from the reduction of the oxides, which in this case had an onset of as low as 500°C (see Figure 7), followed by shrinkage due to pore removal and final densification. The differential shrinkage between the two components is managed by a complex sintering schedule. Success is demonstrated in Figure 8, where a YSZ electrolyte and Inconel 617 interconnect hybrid structure have been successfully co-sintered. Concerns still exist in the area of bonding and migration of elements across the material boundaries during sintering or operation. It is a delicate balance between sufficient reaction to create adhesion and widespread reaction zone formation. In the mean time, thermo-mechanical stress of this hybrid honeycomb SOFC is being modeled, for thermal environments typical to start up and steady state operation.

**Electrodes**

The anode at this point has remained a nickel-ceria cermet. The nickel is introduced as nickel oxide, which is purchased from Aldrich. The ceria is samarium-doped (SDC) with the composition of Sm$_{0.2}$Ce$_{0.8}$O$_{2-δ}$, which is made by the glycine nitrate process. The slurry produced from these materials is passed through the anodic channels. The channels are blown clear and the slurry dried to prevent puddling and channel blockage before subsequent layers are added. Anodes are fired at 1100 to 1200°C.

Cathodes are deposited in a similar manner. The resulting deposited electrodes in an extruded cell can be seen in Figure 9. The use of multiple coatings allows the possibility to tailor the composition and microstructure of the electrode through its thickness. Studies of functionally graded electrodes starting from LSM-GDC and finishing in LSCF have been shown by us to provide superior performance for the cathode. The
functional grading also appears to alleviate potential problems with the thermal expansion differences between YSZ and LSCF. Further studies involving gradation of microstructure is on going. Structure such as those seen in Figure 10 are suggested for the promotion of gas phase transport and electronic conduction in the top layers with high surface area for oxygen exchange and catalysis in the layer closest to the electrolyte.

CONCLUSIONS

A new method of fabricating solid oxide fuel cells is in the development stages. The method promises the possibility of high power density stacks from a single extrusion process. Gas manifolding and electrode application have been successfully accomplished on electrolyte-only honeycomb extrusions. Stacks consisting of alternating layers of interconnect and electrolyte have been extruded and fired with good success.

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REFERENCES

1. S. de Souza, S. Visco, L. De Jonghe, Solid State Ionics, 98, (1997).
2. C. Xia, W. Rauch, W. Wellborn, and M. Liu, Electrochem. and Solid-State Letters, 5, (2002).
3. M. Sahibzada, B. Steele, D. Barth, R. Rudkin, and I. Metcalfe, Fuel, 78, (1999).
4. T. Tsai and S. Barnett, Solid State Ionics, 98, (1997).
5. J. W. Kim, A. Virkar, K. Z. Fung, K. Mehta, and S. Singhal, J. Electrochem Soc., 146 (1999).
6. S. C. Singhal, Solid State Ionics, 135, (2000).
7. N. Minh, A. Anumakonda, B. Chung, R. Doshi, J. Ferrall, G. Lear, K. Montgomery, E. Ong, L. Schipper, and J. Yamanis, Fuel Cells Bull., 6, (1999).
8. S. Linderoth and P. H. Larsen, Mat. Res. Symp. Proc., 575, p. 325 Materials Research Society, Warrendale PA USA (2000).
Figure 1. Conceptual drawing of fuel cell stack formed from single extruded component.

Figure 2. Manifolding schematic for Honeycomb SOFC.
YSZ-8%
Cell = 1900 μm
Wall = 280 μm

Figure 3. Extrusions of YSZ electrolyte honeycomb monolith showing uniformity of walls and manifolding.

Figure 4. Details of die to produce 4 x 4 extruded honeycomb.
**Figure 5.** Barrel attachment for new die to extrude multiple layers from different feedstock.

**Figure 6.** Hybrid extrusion of YSZ and Inconel 617.
Figure 7. Shrinkage curves for YSZ and Inconel 617 during sintering process.

Figure 8. Photo of unsintered and sintered hybrid structure demonstrating validity of hybrid extrusion technique.
Figure 9. Photo of honeycomb section showing internal electroding performed by slurry coating.

Figure 10. Graded microstructure electrode produced by multiple coating techniques.