SOLID OXIDE FUEL CELL RESEARCH AND DEVELOPMENT PROGRAM AT THE CONNECTICUT GLOBAL FUEL CELL CENTER

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ABSTRACT

This paper describes some of the research programs being undertaken in the area of solid oxide fuel cells (SOFC) within the newly formed Connecticut Global Fuel Cell Center at the University of Connecticut. These include, but are not limited to, fabrication (by extrusion) and testing of intermediate temperature micro-tubular based SOFC systems; mechanical testing of electrolytes and cells in a number of different morphologies; electrical properties of intermediate temperature electrolyte materials including ceria and perovskite-based systems; issues affecting the reliability and durability of SOFC cells, stacks, and systems; and modeling aspects including micro and macro modeling.

INTRODUCTION

Overview of the Connecticut Global Fuel Cell Center

The Connecticut Global Fuel Cell Center (CGFCC) is a newly established partnership between the state of Connecticut, Connecticut industry and the University of Connecticut. The mission of the CGFCC is to be a “leading world-class institution in fuel cell research, design, education and training, and product development.” The Center will not just focus on one fuel cell technology or market, but will provide a source of technical strength capable of addressing the multitude of issues across the fuel cell product platform.

The CGFCC began in December 2001 as a partnership between the School of Engineering at the University of Connecticut, Connecticut Innovations, and Connecticut industry. This endeavor arose from the confluence of several key factors: Connecticut’s existing strength in the commercial development of fuel cell products (both OEMs and their suppliers), and the University’s strong core of innovative research in fuel cell and related technologies.

The CGFCC has a dedicated, state-of-the-art, 16,000 square foot facility, shown in Fig. 1, which serves as the focal point for multidisciplinary fuel cell research. This building was completed during 2001 through $2M in funding from the Department of Commerce and the Economic Development Authority combined with $670K from the University of Connecticut. The research portion of the building consists of 8 laboratories; four are...
approximately 1,000 sq. ft. high bay areas, and four are 900 sq. ft. wet chemistry laboratories.

Although the CGFCC covers research and development in a wide range of fuel cell technologies, this paper will examine a number of programs being undertaken in the solid oxide fuel cell group within the CGFCC.

Figure 1. Connecticut Global Fuel Cell Center Building.

CURRENT SOLID OXIDE FUEL CELL PROGRAMS AT THE CGFCC

The small-scale tubular solid oxide fuel cells (SOFCs), as investigated in the CGFCC (1-4), have a number of advantages over planar designs, including excellent thermal shock properties giving rapid start-up ability, and high mechanical integrity. To reduce SOFC operating temperature and, hence, increase the energy efficiency, decrease materials costs, and optimize the internal reformation temperature, alternative ionic conductors could replace the conventional ZrO2-based electrolytes. The major focus of the SOFC group is to determine new electrolyte systems for intermediate temperature (IT) SOFC’s. Herein some properties of these IT materials for small scale tubular SOFCs will be examined.

Fabrication, Properties and Development of a Novel Intermediate Temperature Electrolyte for Solid Oxide Fuel Cell Applications

Perovskite based systems (ABO3) have been considered as alternative options as electrolytes in intermediate temperature SOFC applications (5). Recently, doped-LaGaO3, first reported by Ishihara et al. (6), has been shown to have a very high oxygen ion conductivity (7,8); La0.8Sr0.2Ga0.85Mg0.15 was reported as having a conductivity of 0.14 S/cm at 800°C. LaGaO3 has also been found to be almost a pure oxygen ion conductor from PO2 = 1 to 10-20 atm. (9). Thus, the material has great potential as an electrolyte in a SOFC system.

Although much research has been undertaken on the electrical properties of the material, negligible work has been performed to look at its long term stability and its mechanical integrity (both short and long term) under the conditions prevalent in the SOFC. This is particularly so for the small-scale SOFC system, where high thermal stresses are
expected, due to the nature of the design (fuel is passed through the tube, and is electrochemically oxidized along its length causing a high thermal gradient and, potentially, mechanical failure particularly where the design requires the fuel cell tube to have a hot zone (where the reaction occurs) and a cold zone (outside the fuel cell stack)). A typical micro-tubular SOFC is described in Fig. 2, designed within the CGFCC, where the fuel is passed through the tubes and the oxidant (usually air) is present on the outside of the tube.

![Diagram of micro-tubular SOFC single cell](image)

Figure 2. Schematic of micro-tubular SOFC single cell, based on a doped perovskite system.

![Diagram of extrusion device](image)

Figure 3. Schematic diagram (a), and photograph (b) of the extrusion device.

The single cell tube described above is made by extrusion of the doped perovskite extrudate, which is a relatively low-cost process. The extruded electrolyte forms the structural support of the tubular SOFC, onto which a thin cathode layer is deposited. A thin catalytically active anode layer is then painted on the inside of the electrolyte tube. Raw powders are used to synthesize the different perovskite morphologies. Initially, doped-LaGaO$_3$ was investigated. However, further oxide ion conducting perovskite materials will also be examined in the future. Initially, commercially available La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (LSGM) powder is mixed with a lubricant, a pH control agent, a binder, and a liquid medium (initially distilled water), in a sigma blade mixer until the mix forms a dough. Times of mixing depend on the perovskite being studied (it is a function of the ceramic particle morphology). A degassed and homogeneous dough is then extruded into tubes using a 16 ton ram extruder under various ram pressures. The extrudate is sintered at various temperatures for various times in an electrical furnace in

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air. The equipment used in the fabrication of the electrolyte tubes is shown in Fig. 3. A number of different sized tubes are fabricated in order to study the effect of wall thickness on their mechanical performance. Samples are also made into bars of fixed dimensions to investigate the 3-point modulus of rupture (MOR) values for the material, as a base line to compare with the mechanical properties of the tube (where no ASTM standard is available).

Scanning electron microscopy and metallurgical microscopy are employed to inspect the microstructure and crystal structure of the sintered products, as well as the particle morphology of the powders. Particle size analysis and surface areas analysis (BET) of the powders is also undertaken.

As well as tubes, the mechanical integrity of a full SOFC single cell can also be determined. Single cells, also constructed for mechanical testing, consisting of an anode, the electrolyte, and a cathode, are fabricated. Anodes were formed from NiO, Co (II, III) oxide, NiO with 8 mol% yttria-stabilized zirconia (50:50 vol%), and NiO with doped-ceria. Cathode materials of La and Sm based cobaltites are selected and compared with the conventional La$_{0.8}$Sr$_{0.2}$MnO$_{3.4}$ (LSM). Anodes and cathodes are made into slurries in order to apply them onto the electrolyte support tubes. The anode slurry is dip coated inside the electrolyte tubes by sucking the slurry into the tubes using a syringe-pipe configuration, and fired. Cathode slurries are brush painted onto the electrolyte tubes after completing the anode-firing regime, and sintered.

MOR results of the lanthanum gallate materials are determined from bars polished and chamfered using SiC media. The MOR is realized using a standard 3-point bend apparatus and an Instron Universal Testing Machine. A high temperature furnace is available to test the samples at temperatures ranging from room temperature to 1000°C and under different gaseous atmospheres (typically air, hydrogen and methane). Other perovskite systems (as and when determined) are also examined. Fracture toughness is determined using the standard indentation technique (using a Vickers micro-indentor). High temperature fracture toughness can also be realized from examination of the high temperature MOR fracture surface examined under the SEM.

The strength of the tubes (both the single cells and uncoated tubes) can be realized using an apparatus described in Fig 4. The tube is seated into a pressurized rig, and a liquid medium (typically water) pressurizes the tube until it fails. The force required to fracture the tube can be used to determine the strength of the material. High temperature properties can also be realized using the apparatus and a small-scale furnace. With an understanding of the effect of mechanical properties on the microstructure, the integrity of the cell can be realized by using a modeling package, such as ANSYS. Other data, including the thermal expansion coefficient (TEC), the density and thermal coefficient, can also be determined for each material to enable a fuller picture to be realized. Computer modeling can be used to determine the stress development for a range of heating rates and material property values. The ANSYS finite element modeling environment can be used to generate the model with a batch interface employed to generate results. The program can be used to determine how well the material will behave in a “real” fuel cell environment over finite periods of time. The advantage of using a FEA computer model is that the data can be realized from the measurements and used to determine how well a fuel cell stack will behave, without going to the expense of
building a number of designs. This work will provide invaluable data for the SOFC program as a whole, as it will finally allow a stack to be built with preceding knowledge about its potential performance.

![Apparatus developed to measure the rupture strength of tubes and tubular single cells.](image)

**Figure 4.** Apparatus developed to measure the rupture strength of tubes and tubular single cells.

Typical voltage/power density-current density curves of a state-of-the-art single SOFC (lanthanum cobaltite cathode/LSGM electrolyte/doped ceria interlayer/Ni/YSZ anode) system is shown in Fig. 5, running off humidified-hydrogen at various temperatures and running times (given in hours in the legend). The cell performance was observed to increase over time. Repeatable power of 2.5-3 W per cell, with 0.55 mm thick electrolyte, was obtained. A maximum power density of 350 mW/cm² for the 0.55 mm thick electrolyte cell and 482 mW/cm² for a 0.22 mm thick electrolyte cell, were achieved.

Fig. 6 shows a comparison of the modulus of rupture (MOR) of some extruded electrolyte materials (rods) tested at room temperature and at high temperature in air. In general, for all of the three electrolyte materials (LSGM, CGO (gadolinia doped ceria), and 8YSZ) examined, the mechanical strength decreases with an increase in temperature. The MOR of LSGM electrolyte is smaller than that of CGO and YSZ at the same temperature. At temperatures higher than 800°C, the MOR of LSGM and CGO decreased rapidly, while the MOR of YSZ at 1000°C is greater than that at medium temperatures (600°C and 800°C). The latter trend for YSZ was also observed by Minh (10) and Mori et al. (11); however, the reason is not apparent and is the subject of much scrutiny. Burst failure test results of some tubular electrolytes are listed in Table 1. Compared to the bending strength of the same extruded material, the burst strength is much smaller, but a similar trend in strength is observed, and again YSZ shows the greatest burst-strength amongst the three electrolytes. The burst test is an efficient method to detect the weakest point along the test specimen. This is because the breaking pressure is distributed evenly over the whole volume in the tube, and therefore a greater volume of defects can be detected.
Figure 5. Cell voltage and power density as a function of current density at 800°C and various operation times. The cell consists of air, LSC/LSGM/SDC/Ni, H₂/O. LSGM thickness was 0.55 mm.

Figure 6. Modulus of rupture of the extruded LSGM, CGO, and YSZ electrolyte materials, tested at room temperature and high temperature.

Table 1. Burst Strength Test data for LSGM, CGO and YSZ tubes.

|       | MOR MPa | Burst strength MPa | Burst strength after furnace thermal cycling between 1300°C and room temperature, MPa |
|-------|---------|--------------------|----------------------------------------------------------------------------------|
|       |         |                    | 22 times                                                                        | 30 times |
| LSGM  | 287     | 40                 | 30                                                                               | 25       |
| CGO   | 322     | 63                 | -                                                                                | -        |
| YSZ   | 323     | 127                | 104                                                                              | 82       |
Overall, the mechanical strength of LSGM is weaker than either YSZ or CGO prepared in this work. According to the Hall-Petch relationship, for the same material, the finer the grain size, the stronger the material will be (all else being equal). In this work, the optimum theoretical density was found for grain sizes of: 10-20 µm (LSGM), 4-10 µm (CGO), and 1-5 µm (YSZ). However, no relationship between strength and grain size is observed between these materials, and thus the variation in strength is due to material factors and not solely to grain size differences. These results, therefore, can be used as a comparative study for three dense fuel cell electrolyte materials, and not as an absolute comparison.

**Reliability and Durability of SOFC Systems**

Another part of the SOFC team at the CGFCC is concerned with issues that affect the reliability and durability of SOFC cells, stacks, and systems. One of those issues is the effect of manufacturing on the properties and integrity of the cells. Because of the large differences in the sintering temperature, working temperature, and room temperature, large thermal stresses may exist as a result of relatively small differences in coefficients of thermal expansion (CTE) among the cathode, anode, electrode, and interconnect materials. Reifsnider and Huang (12) have considered delamination and transverse cracking failure of co-sintered layered ceramic thin films. The driving forces for failure, free edge peel stress and strain energy release rate, due to thermal stresses were estimated using simple engineering approaches for planer systems. The magnitudes of these driving forces were expressed as functions of the initial CTE mismatch. Trade-off studies for geometric factors and material properties as a function of temperature were used to suggest methods to control specific failure modes in these layered composite systems. Reifsnider and Huang are also considering the fact that even when a close match of the layer thermal properties is achieved, internal stress can still exist due to the non-uniform distribution of temperature, oxygen partial pressure, and current density which exists during operation. Transient processes during start-up and shutdown can also result in large internal stresses.

In order to correctly estimate the internal stresses in the system, and the chance that those stresses will cause localized fractures, the local properties of the material must also be determined. However, mechanical properties, such as the stiffness and strength, change with prolonged high temperature operation, especially in the presence of aggressive gases and electrochemical currents. This issue is also being addressed by the CGFCC team (13).

Indentation methods have been developed to determine the local toughness of in-situ layers in fuel cells. Micro-indentation has the advantage of providing toughness data on the correct scale (of a few microns) so that “bulk” properties of the individual layers can be determined (Fig. 7). It was found that nano-indentation data were more indicative of surface properties, in this context. Reifsnider et al. (13) developed a method of obtaining such indentation data from the exposed edges of SOFC cells that exactly matches data from the surface of the individual layers before they are bonded together. This unique capability enables “before and after” studies to determine the changes in mechanical properties brought about by aging.
Another reliability issue being considered is the need for modeling. A fuel cell is a functional material system involving processes in a number of physical domains: the electrochemical reaction at electrode-electrolyte interfaces, the transport of fuel and oxidant through channels, diffusion of reactants through porous electrodes to reaction sites, the generation and diffusion of heat, the equilibrium of internal stress, and others. These processes are governed by a large system of coupled integral-differential equations which together determine the characteristics and performance of a SOFC. In this context, one must use multiphysics models to represent the total corpus of physics processes that are responsible for the function of a SOFC. Such models are an essential basis for failure analysis and long-term performance prediction. The CGFCC team has developed multiscale methods of formulating and solving such an equation set (14). Among the results of that effort is the capability to calculate local gradients in temperature and electrochemical activity that contribute significantly to property evolution and degradation. These coupled multiphysics models represent both the steady and transient characteristics of a SOFC. Solution of the sub-models simultaneously enables us to correctly represent the in-situ performance of a SOFC. To predict the long-term stack performance, one must know the local material degradation state, which depends on the history of local intensity variables (temperature, current density, etc.). The local operation variables can only be obtained through proper solution of the coupled multiphysics models. In order to extend the solutions to allow long-term predictions, the change of material state with time must be included (15). Reifsnider and Case (16) have developed a modeling approach for life prediction under such complex conditions. This modeling approach is based on the fact that the state of local material degradation can be represented by scalar performance metrics and the rate of degradation of these metrics is function of local intensity variables and their entire history. The approach allows a natural treatment of degradation from multiple sources and processes and has been successfully used to treat combined damage problems due to fatigue and creep for composite material systems, including sequence effects (c.f. (17)). The detailed philosophy (and MRLife code) is explained in a treatise recently published by Reifsnider and Case (16).
A final reliability and durability issue being addressed by the CGFCC team is the need for microstructural modeling, especially the need for models of the local geometries and properties of constituent layers in a SOFC and their changes with time. The greatest advantage of such direct representations of all of the essential local details of the topology (including interfaces) and properties is that it enables us to directly calculate global properties such as stiffness, strength, and conductivities of "real" material systems used in SOFCs, and brings the real world of manufacturing variables to the global representations of the performance of fuel cells. For this purpose, our team has constructed a new approach to the modeling of porous heterogeneous media. An example is shown in Fig. 8. (15). This modeling approach has the capability to capture truly random topological effects, and has been validated as a method of predicting mechanical stiffness of randomly porous materials (15). Work continues on this important capability.

| Traditional continuum approach:                                                                 | Multi-scale "FIBNET" Approach:                                                                 |
|---------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| Misses intricate interface features that actually dictate the performance of the functional material, e.g., the TPB length. | Can include the finite gradient transition of certain features across the interface           |
| Generates artificial singularities                                                          |   - Avoids artificial singularities                                                          |
|                                                                                             |   - May potentially relate to microscopic observables                                       |

Figure 8. Advantages of new "FIBNET" model for the representation of the local geometry and global properties of heterogeneous porous materials with internal gradients.

CONCLUSIONS

The SOFC team within the Connecticut Global Fuel Cell Center is looking at, but not limited to, a number of issues relating to the solid oxide fuel cell. Two issues discussed here were the physical and mechanical properties of some intermediate temperature SOFC electrolytes from the perspective of a micro-tubular system, and reliability issues relating to the SOFC stack.
REFERENCES

1. K. Kendall and M. Prica, in *Proceedings of the First European Solid Oxide Fuel Cell Forum*, U. Bossel, Editor, p. 163, Lucerne, Switzerland, (1994).

2. M. Prica, T. Alston, and K. Kendall, in *SOFC-V*, U. Stimming, S. C. Singhal, H. Tagawa, and W. Lehner, Editors, *PV 97-40*, p. 619, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).

3. Y. Du, N. M. Sammes, and G. A. Tompsett, *J. Eur. Ceramic Soc.*, 20 (7), 959 (2000).

4. C. Hatchwell, N. M. Sammes, I. W. M. Brown, *Solid State Ionics*, 126, (1999) 201.

5. R. Maric, S. Ohara, T. Fukui, H. Yoshida, M. Nishimura, T. Inagaki, and K. Miura, *J. Electrochem. Soc.*, 146, 2006 (1999).

6. T. Ishihara, H. Matsuda, and Y. Talita, *J. Am. Chem. Soc.*, 116, 3081 (1994).

7. K. Huang, M. Feng and J.B. Goodenough, *J. Am. Chem. Soc.*, 79, 1100 (1996).

8. K. Huang, R. S. Tichy, and J. B. Goodenough, *J. Am. Ceram. Soc.*, 81, 2565 (1998).

9. J. Drennan, V. Zelizko, D. Hay, F. T. Ciachchi, S. Rajendran,, and P. S. Badwal, *J. Mater. Chem.*, 7, 79 (1997).

10. N. Q. Minh and T. Takahashi *Science and Technology of Ceramic Fuel Cells*, Elsevier Science B.V. Amsterdam, (1995).

11. M. Mori, T. Abe, H. Itoh, O. Yamamoto, Y. Takeda, T. Kawahara, *Solid State Ionics*, 74, 157 (1994).

12. K. Reifsnider, X. Huang, X., in *Proceedings of the American Society for Composites 16th Annual Technical Conference (CD)*, M. W. Hyer and A. C. Loos, Editors, paper No. 224, CRC Press, Boca Raton, FL, (2001).

13. H. Halverson, S. W. Case, K. Reifsnider, and K. An, “Fuel Cell Technology Development Program,” contractors’ report to McDermott Technologies, Inc., September 1, 2002.

14. K. L. Reifsnider, X. Huang, and N. Olsen, in *Proceedings of the 7th Japan International SAMPE Symposium and Exhibition (JISSE-7)*, T. Ishikawa and S. Sugimoto, Editors, p. 559 Tokyo, Japan, (2001).

15. K. L. Reifsnider, X. Huang and V. Vinjamooiri, in *Proc. Intl. Conf. On New Challenges in Mesomechanics*, R. Pyrz, et al., Editors, p. 439, Aalborg University, (2002).

16. K. Reifsnider and S. Case, *Damage Tolerance and Durability in Material Systems*, John Wiley & Sons, (2002).

17. K. Reifsnider, S. Case, and N. Iyengar, in *Proceedings of the 1998 Thirty-Ninth AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference and Exhibit and AIAA/ASME/AHS Adaptive Structures, AIAA-98-1739*, p. 352, American Institute of Aeronautics and Astronautics, (1998).