IV.A.11 Reliability and Durability of Materials and Components for Solid Oxide Fuel Cells

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Objectives

- To support the Solid State Energy Conversional Alliance (SECA) industrial teams towards the development of reliable and durable solid oxide fuel cells (SOFCs).
- To support SECA Core Technology Program (CTP) modeling efforts by establishing material property databases.
- To establish failure criteria for SOFC materials and components associated with thermal fatigue and other degradation mechanisms.
- To determine the fracture behavior of SOFC materials and their interfaces.

Accomplishments

- Developed a test procedure to quantify the fracture toughness of interfaces between cathode contact paste and metallic interconnects.
- Assessed the effect of sintering temperature and sintering time on the fracture toughness of interfaces between cathode contact paste and metallic interconnects.
- Contributed to the preparation of a design guide for solid oxide fuel cells.

Introduction

The steady decrease in performance, as determined by steady decreases in voltage with time, exhibited by some planar SOFCs has been associated with processes that occur on the cathode side of the cell. Some of these processes result from the interaction between the cathode and the interconnect material [1].

Interconnect materials for SOFC fall into two categories: conductive ceramics for operation at high temperature (900 to 1,000°C) and metallic alloys for lower temperature operation. Metallic interconnects have the advantage of higher electronic and thermal conductivity, higher ductility, and better workability [2]. However, even at lower operating temperatures, design requirements for metallic interconnects are challenging because they must maintain uniform contact (usually requiring some pressure) with the electrodes and in the case of the cathode, preserve low contact resistance while exposed to oxidizing conditions [3].

To reduce interfacial resistance, electrical contact layers are often applied between the cathode and the metallic interconnect during assembly of SOFC stacks. The contact material must be chemically compatible in oxidizing conditions with both the interconnect material and the cathode because reactions could result in the formation of phases that could lead to an increase in contact resistance or thermal expansion mismatches that could lead to delamination. It is common to sinter the contact layer during the first heating cycle of the stack in which case it is important that the contact material possesses appropriate sintering activity to increase contact area and thus decrease contact resistance. However, excessive sintering could eliminate porosity in the contact layer and block airflow to the cathode/electrolyte interface, thus affecting cell performance [4].

The objective of this study is to identify and utilize test techniques to determine the physical and mechanical properties of cathode contact paste materials and the mechanical properties of the interfaces that exist among the cathode, the contact paste and metallic interconnects or coated metallic interconnects in SOFCs. The properties obtained in this study will support ongoing efforts to develop models of the thermomechanical and electrochemical behavior of SOFCs. This study will also provide insight into the mechanisms responsible for the degradation of SOFCs and in turn, strategies to overcome these limitations, particularly when SOFCs are subjected to service conditions for long periods of time, including cyclic operation.

Approach

Test specimens were prepared by cutting strips of the metallic alloy Crofer 22 APU (ThyssenKrupp VDM) by electric discharge machining followed by grinding using 1200 grit silicon carbide sand paper to obtain beams with dimensions of 30 mm x 2.5 mm x 0.2 mm and 15 mm x 2.5 mm x 0.2 mm. One end of the short beams was impregnated with a solution of 97% BN, 1% MgO and 2% SiO_2 to prevent wetting in subsequent steps and to facilitate the initiation of a delamination crack. A layer of lanthanum strontium manganate (LSM) contact paste (LSM-20 Ink, FuelCellMaterials) was applied on one side of a 30-mm long beam and the two 15-mm long beams were placed on top of the coated beam. A fixture was fabricated to ensure the alignment of the beams and to control the thickness of the LSM contact paste. Test specimens were allowed to dry in air followed by heating at a rate of 3°C/min to various sintering temperatures and for various periods of time. A sharp blade was used to introduce a notch between the two 15-mm long beams. The edges of some test specimens were polished according to standard metallographic techniques to facilitate microstructural observations after the test. Figure 1 illustrates the sequence of steps followed to prepare the test specimens.

The test specimens were evaluated in four-point bending following a modified version of the test method of Charalambides et al., which allows the determination of the critical energy release rate at bi-material interfaces by means of four-point bending under approximately equal shear and normal displacement conditions [5-6]. This test method is attractive for this application because it uses a relatively simple sample geometry and a well-established testing procedure. The sample geometry consists of a sandwich structure comprised of metallic interconnect layers bonded by a layer of contact paste as described above. The top metallic interconnect layer suppresses the segmentation of the brittle contact paste and increases the stored energy in the layer and therefore the driving force for delamination [7].

The tests were carried out at a constant crosshead displacement rate of 0.1 µm/second using an electromechanical testing machine and a four-point bending fixture with a support span of 20 millimeters and a loading span of 10 millimeters. The load versus displacement data were collected during the test to subsequently calculate the energy release rate. Test specimens with different sintering temperatures and sintering times were evaluated. Also, the effect of the thickness of the LSM contact paste was investigated.

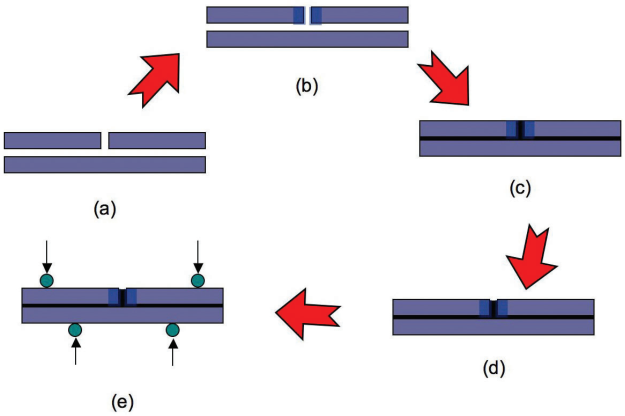

FIGURE 1. (a) Crofer 22 Beams; (b) Application of BN to Facilitate Crack Initiation; (c) Application of LSM Contact Paste Followed by Sintering; (d) Introduction of Notch in LSM Contact Paste; (e) 4-point Bend Testing of Test Specimen

The energy release rate was determined according to Equation (1):

$$G = \frac{(1 - v^2)M^2}{2E}\left(\frac{1}{I_2} - \frac{1}{I_c}\right) \tag{1}$$

$$M = \frac{Pl}{2b} \tag{2}$$

$$I_c = \frac{h_1^3}{12} + \frac{h_2^3}{12} + \frac{h_1 h_2 (h_1 + h_2)}{4} \tag{3}$$

$$I_2 = \frac{h_2^3}{12} \tag{4}$$

where G is the energy release rate, P is the applied load, b is the width of the bars (2.5 mm), h_1 and h_2 are the thickness of the top and bottom bars (0.2 mm), l is the distance between the inner and outer pins (see Figure 2), M is the applied bending moment and E and v are the elastic constants of the metallic interconnect material.

Results

Figure 3 illustrates a typical load versus crosshead displacement curve obtained from one of these tests. In all cases the load increases linearly until a vertical crack forms in the LSM paste at the root of the notch introduced with a sharp blade. That event is followed by a sudden load drop, which corresponds to the growth of a crack across the LSM layer and its deflection into one of the interfaces between the LSM layer and the Crofer 22 APU layers. The load plateau in the load versus

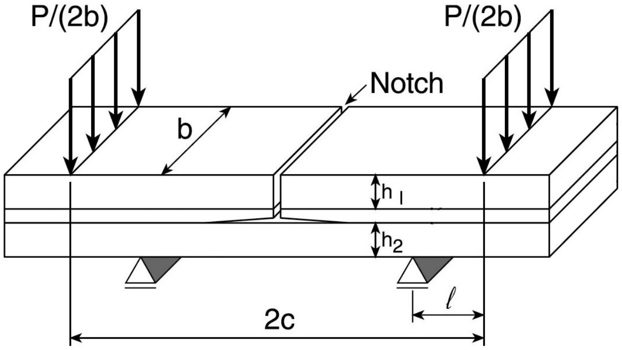

FIGURE 2. Schematic of Test Configuration [5-6]

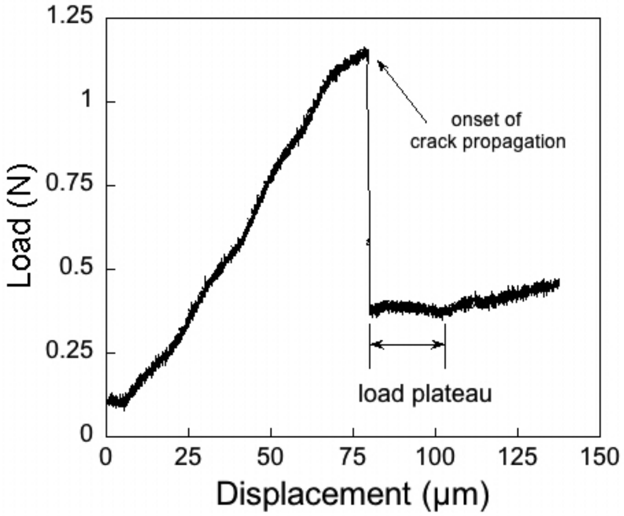

FIGURE 3. Typical Load Versus Displacement Curve Obtained from the Interfacial Evaluation of a Test Specimen Comprised of Crofer 22 APU Interconnects and LSM Contact Paste Sintered at 900°C for 1 Hour

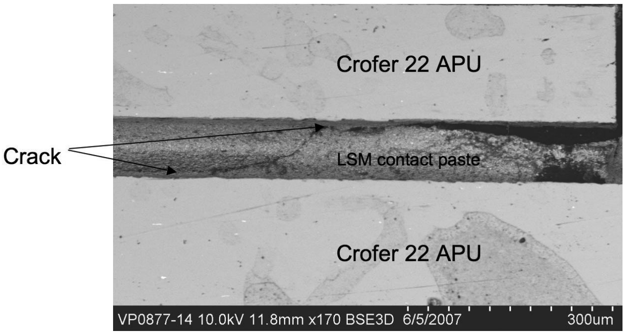

FIGURE 4. Scanning Electron Micrograph of Test Specimen Illustrating Path of Crack Propagation

displacement curve corresponds to the stable growth of the interfacial crack and that is the value of the load used for the calculation of the energy release rate. Upon further machine crosshead displacement, the crack reaches the loading points and is arrested.

The test specimens were examined after the mechanical tests using optical and scanning electron microscopy. It was found that cracks propagated through the LSM contact paste layer and were deflected to the interface between the LSM contact paste and the Crofer 22 APU layers as illustrated in Figure 4. Similar observations were obtained from the analysis of the two halves of test specimens after complete separation, which revealed regions of bare metal and islands of LSM contact paste.

It was found that the interfacial energy release rate increased with both the LSM contact paste sintering temperature and sintering time as shown in the plot in Figure 5. These results are consistent with the fact that the density, and hence the strength, of the LSM contact paste increase with sintering time and temperature. It was also found that the energy release rate increased with the thickness of the LSM contact paste layer. This result was unexpected but work is in progress to prepare and evaluate test specimens with a wider range of LSM contact paste thickness values to further understand these trends.

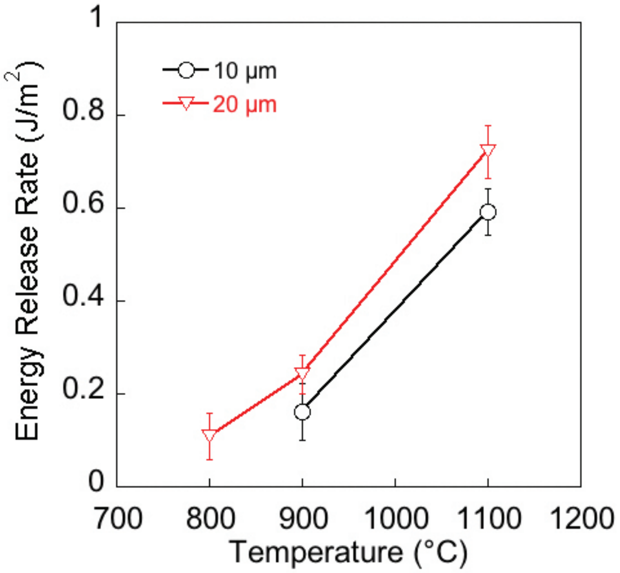

FIGURE 5. Effect of Sintering Temperature on the Interfacial Energy Release Rate Test Specimens Comprised of Crofer 22 APU Interconnects and LSM Contact Paste

Current work in collaboration with researchers at Pacific Northwest National Laboratory (PNNL) is focused on the characterization of systems that include metallic interconnects that have been coated with $(Mn,Co)_3O_4$ spinel to prevent Cr volatilization. These measurements are being complemented with *in situ* impedance measurements and observations of the cracking processes.

Conclusions and Future Directions

A technique was developed to determine the energy release rate of interfaces between LSM contact paste and Crofer 22 APU metallic interconnects. Results were obtained for test specimens that were processed at different sintering temperatures and for different periods of time. It was found that the interfacial energy release rate increases with both sintering temperature and sintering time. It was also found that cracks initiated in the LSM contact paste and were deflected to the interface between the contact paste and the metallic interconnect. Current and future work is focused on using these techniques and analysis to characterize the interfacial properties of other systems that include $(Mn,Co)_3O_4$ spinel coated metallic interconnects and other contact paste compositions.

FY 2007 Publications/Presentations

1. E. Lara-Curzio, R. M. Trejo, C. Cofer , "Dimensional Stability of Ni-YSZ at Elevated Temperatures," Presented at the 31st International Conference & Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, January 22–26, 2007.

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2. W.J. Quadakkers, H. Greiner, M. Hansel, A. Pattanaik, A.S. Khanna, W. Mallener, "Compatibility of Perovskite Contact Layers Between Cathode and Metallic Interconnector Plates of SOFCs," *Solid State Ionics* **91** (1996) pp. 55-67.

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