V.J.6 Silicon-Based Solid Oxide Fuel Cell for Portable Consumer Electronics*

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*Congressionally directed project

Objectives

Increase micro-electro-mechanical systems (MEMS) solid oxide fuel cell (SOFC) array power density and lifetime through process and design changes that will:

- Significantly improve the throughput and repeatability of the electrode manufacturing process.
- Improve the average power density of the SOFC array by 50%.
- Improve chip-level vacuum sealing to support operation at 800°C.
- Allow fabrication and test of SOFC devices that demonstrate realized improvements over current design.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is directed at the development of improved micro-SOFC chips and high-volume compatible manufacturing processes. The power, lifetime, and manufacturability improvements will be applied toward portable fuel cell systems that meet the following DOE 2010 consumer electronics targets:

- Energy density: 1,000 Wh/L
- Lifetime: 5,000 h

Accomplishments

- Established a scalable, automated fuel cell electrode dispense platform with a 10X improvement in repeatability.
- Improvements in stack array electrode adhesion increased SOFC energy density by 85%.
- Modification of the thin film stack on the silicon support structures provided an increase in operating temperature from 700°C to 750°C, resulting in a 30% power improvement.
- Incorporation of these improvements into a full SOFC chip assembly provided a 250% power improvement over the best demonstrated chip at the start of this project.

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Introduction

Lilliputian Systems Inc. (LSI) is developing a novel miniature fuel cell for the consumer portable power market. LSI's fuel cell uses efficient SOFC technology, is manufactured using MEMS fabrication methods, and runs on high energy fuels, such as butane, hydrogen, or ethanol. The company's breakthrough Fuel Cell on a Chip™ technology enables a form-factor battery replacement for portable electronic devices that has the potential to provide an order-of-magnitude run-time improvement over current batteries.

This Department of Energy funded project focused on accelerating the commercialization and market introduction of this technology through improvements in fuel cell chip power output, lifetime, and manufacturability. To achieve these objectives, work was performed to close the gap between the higher power density demonstrated on button cell test structures and that available on stacked array die. A robust, automated electrode fabrication tool was developed to support the increased production rate required to perform array optimization. The causes of limited lifetime at elevated temperature were investigated and improvements to the silicon die coatings were made to allow increased SOFC operating temperature. These improvements were then incorporated into a full SOFC chip assembly to benchmark the overall performance improvements realized.

Approach

Scanning electron microscopy (SEM) images of fuel cell electrode arrays indicated that significant electrode delamination was occurring on the array die. This was believed to be related to stress in the electrode introduced during the drying process. Experiments were performed investigating the effect of variations in the amount of electrode material dispensed per coat, as well as the drying and curing process profiles. In order to support increased production rate required to optimize the array electrode process, an automated electrode dispense tool was developed along with a wafer-level electrode fabrication process.

To increased chip lifetime at higher operating temperatures, glass seal improvements were necessary to reduce reactivity with the silicon support structure. Glass compositional changes, incorporation of barrier layers, and modifications to the die films were investigated.

Results

The energy density achieved on electrode test structures has historically been higher than the energy densities attained on stacked electrode arrays. The more complex physical structure of stacked arrays requires different precursor solutions and process optimization to achieve maximum power density. In order to support the large number of experiments necessary to achieve this optimization, a high-throughput manufacturing process was necessary. This new, high-throughput process also had the requirement of improving electrode consistency.

LSI had investigated commercially available deposition equipment appropriate for producing the SOFC arrays and determined that standard equipment does not have either the accuracy or repeatability necessary for fabrication of high energy density fuel cell arrays. In order to attain the necessary dispense performance, LSI has developed enhancements to equipment built and supplied by Asymtek Inc. An improved dispense volume control system was designed, built, and tested by LSI. Dispense volumetric accuracy and repeatability has been improved by greater than 20X and 10X, respectively (see Figure 1). This has resulted in improved electrode uniformity, faster processing and higher yields. Additional throughput improvement was achieved through implementation of wafer-level processing, which requires less labor than

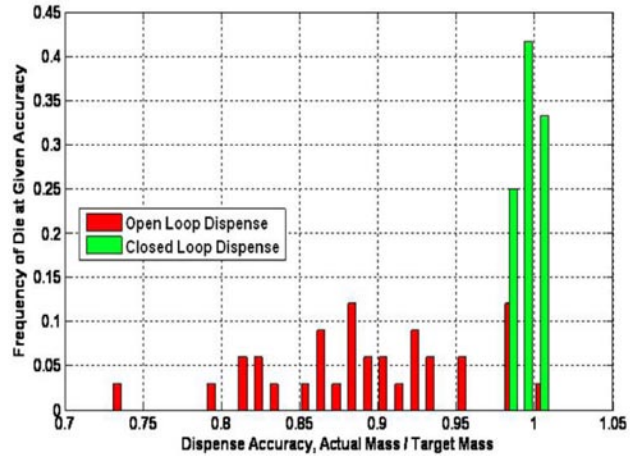

FIGURE 1. Automated Dispense Volume Accuracy With and Without Closed-Loop Control

die-level electrode production. Experiments verifying the equivalency of the wafer-level process have been completed successfully. In addition to providing a solid foundation for the process refinements necessary to increase power density, the improved dispense equipment and wafer-level processing have established a solid platform for rapid scaling to production quantities.

SEM images of the fuel cell electrode arrays have indicated that significant electrode delamination is occurring on the fuel cell die. This is believed to be related to stress in the electrode introduced during the drying process. Experiments were performed which investigated the relationship between the amount of material dispensed per coat and the magnitude of observed delamination. Results have indicated that there is not a significant level of improvement to be gained by this approach. Experiments involving variations in drying temperature and time were performed, which resulted in observable improvements in overall electrode adhesion. Figure 2 shows an 85% increase in array power achieved through process improvements.

Increasing the fuel cell chip operating temperature improves the output power but reduces the chip lifetime. Experiments have shown that the lifetime of the current sealing glass used in the LSI fuel cell chips drops significantly between 700 and 800°C. Cross-section analysis of the glass seals by SEM and energy dispersive spectroscopy (EDS) indicates that chemical changes to the glass composition are occurring at the higher temperatures, and there is evidence that these changes are contributing to the shortened operational lifetime.

Several new glass formulations were created and analytical analyses of these glasses indicated that they crystallize more fully than current glasses, generally indicating higher reliability. Unfortunately due to delays in bringing a new high temperature furnace on-line,

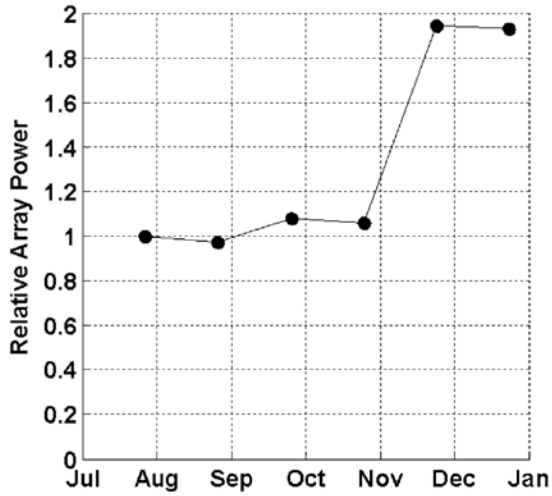

FIGURE 2. Fuel Cell Array Average Power, Normalized to Average Power in July

furnace down-time due to a crucible failure, and glass incompatibility with current paste-making facilities, LSI was not able to evaluate the new glasses in complete fuel cell chip assemblies during the time frame of this project. The new glasses will be evaluated in prototype chips at a future date.

Chemical interaction between the sealing glass and the fuel cell die at elevated temperature has also been investigated through the use of SEM EDS and is a contributor to reduced seal life at higher temperatures. Several proprietary barrier layers were developed and evaluated for suitability in increasing seal lifetime at temperature (see Figure 3). Several of the tested barrier layers showed promise in reducing the reaction between the sealing glass and the silicon fuel cell die; however these materials proved difficult to integrate into the fuel cell die process flow and require substantial redesign of the MEMS chips to incorporate. The insights gained from work performed on barrier layers led to changes in the composition, stress, and thickness of the thin films originally incorporated in the fuel cell chips, and a significant improvement in seal performance was observed, as shown in Figure 4. Although the target operating temperature of 800°C was not fully attained, a significant increase from 700°C to 750°C was realized.

Fuel cell chips were fabricated with both the improved electrodes and the operating temperature enhancements. These devices were tested to benchmark performance, and these changes were shown to increase in fuel cell power by a factor of 2.5X over the maximum power demonstrated at the start of this project. These results are shown in Figure 5. This represents a major step forward in the commercialization of the LSI Micro Fuel Cell Chip technology.

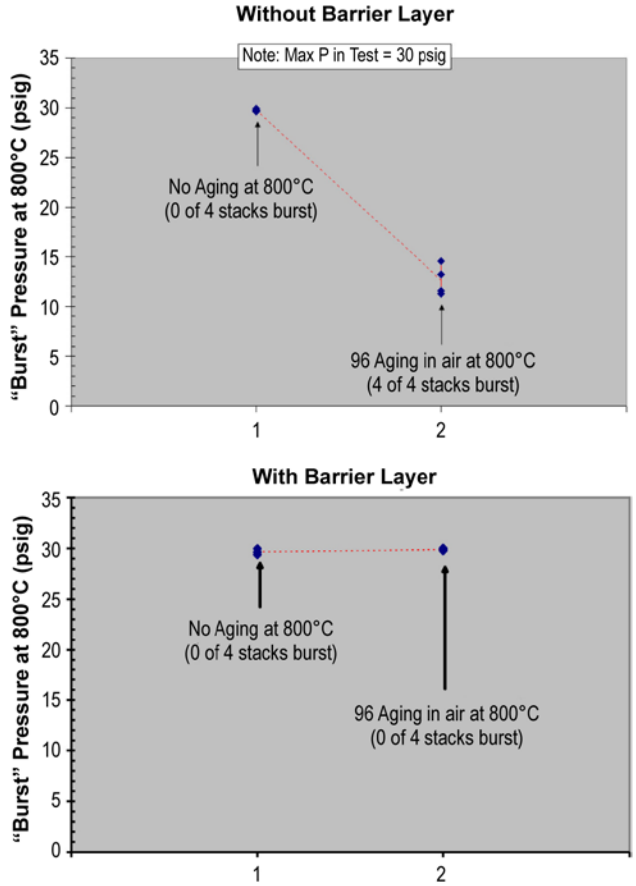

FIGURE 3. Coupon Burst Strength With and Without Barrier Layer (Test pressure limit: 30 psi)

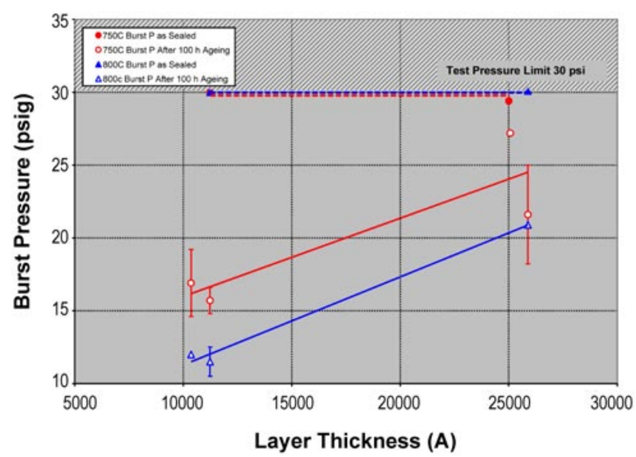

FIGURE 4. Coupon Burst Strength as a Function of Layer Thickness

Conclusions and Future Directions

The LSI MEMS-based micro-SOFC has clearly demonstrated the potential for an order-of-magnitude run-time improvement over the lithium ion batteries

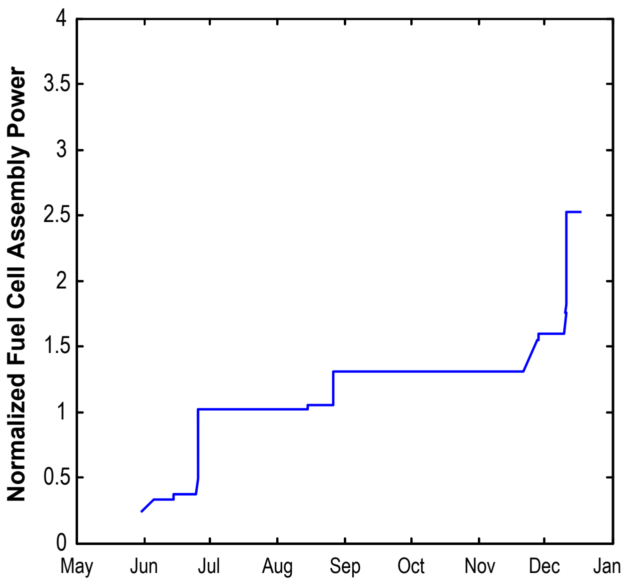

FIGURE 5. Fuel Cell Chip Assembly Power, Normalized to Power in July

used in portable consumer electronics today. The progress made during this project has:

- Provided a scalable, automated fuel cell electrode dispense platform.
- Significantly improved the operating temperature and lifetime of the fuel cell chip.
- Achieved an 85% improvement in array energy density through electrode fabrication process development.
- Achieved a 30% increase in output power due to higher operating temperatures.
- Demonstrated a 2.5X increase in fuel cell chip output power.

Future work will include evaluation of the new glass compositions and revision of the MEMS design to allow incorporation of barrier layers, both to further increase operating temperature and lifetime. Fuel cell energy density will be further improved though continued refinement of the electrode fabrication process and redesign of the silicon support structure to increase fuel cell active area.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review - Washington, D.C. - May, 2009. Presentation FC# 48.