Silicon Based SOFC Chip for Portable Consumer Electronics

Final Technical Report Lilliputian Systems Inc.

Award Agreement

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Project Director

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Executive Summary

Lilliputian Systems Inc. ("LSI") is developing a revolutionary miniature fuel cell for the \$50 billion portable power market. LSI's fuel cell uses efficient Solid Oxide Fuel Cell ("SOFC") technology, is manufactured using Micro Electrical Mechanical System ("MEMS") fabrication methods, and runs on high energy fuels, such as butane and 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. Further, the technology is clean and environmentally-friendly, offering up to a 600% efficiency improvement relative to wall chargers.

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. Specifically, this research has:

- Provided a scalable, automated fuel cell electrode dispense platform
- Improved the operating temperature and lifetime of the fuel cell chip
- Demonstrated a 2.5X improvement in fuel cell chip output power

Task 1.0: Process Transfer to improve Array Energy Density

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. Performing the number of experiments necessary to achieve this optimization required development of a high-throughput manufacturing process. This high-throughput process should also improve the array consistency relative to the manual process historically used to produce arrays.

Significant progress has been made in reproducing the test structure energy density on the arrays which can be integrated into Lilliputian's Micro Fuel Cell Chips. The target goal of a 50% improvement in stacked array power density was exceeded.

1.1. Automatic Deposition of Electrodes

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 development of high energy density fuel cell arrays. Generally, standard equipment with sufficient dispense volume control lacks the positional accuracy and programmability for proper array fabrication. Equipment with sufficient dispense placement accuracy and flexibility does not provide sufficient dispense volume repeatability.

In order to attain the necessary dispense performance, LSI has developed enhancements to equipment built and supplied by the Asymtek Inc. Specifically these retrofits provide a closed loop control over the dispense volume.

The improved dispense volume control system was designed, built, and tested by Lilliputian Systems. Dispense volumetric accuracy and repeatability has been improved by greater than 20X and 10X, respectively. This has resulted in improved electrode uniformity, faster processing and higher yields. In addition providing a solid foundation for the process refinements necessary to increase power density this has established a platform for rapid scaling to production quantities.

Figure 1: Automated dispense volume accuracy with and without closed loop control

1.2. Better Adhesion over Large Arrays

Scanning Electron Microscopy (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 occurring during the drying process. Experiments have been performed which investigate 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 led to observable improvements in overall electrode adhesion. A correlating increase in button cell power of 10 to 20% was also observed.

1.3. Increasing Throughput to Statistically Significant Volumes

Implementation of the improved-accuracy automated dispense equipment, together with added deliveries of raw fuel cell die, have allowed an increase in experimental investigation. Additional improvement has been achieved through implementation of wafer-level processing, which requires less labor than die-level electrode production. Experiments verifying the equivalency of the wafer-level process have been completed successfully. The increased volume of experiments has been instrumental in achieving improved fuel cell array performance.

Task 1 Milestone

Target: Improve the lot average energy density of the SOFC array by 50%.

Achieved: The Task 1 Milestone was exceeded, with average energy density in the best-process lots increasing by over 85%.

Figure 2: Lot average and standard deviation for all experimental lots

Task 2.0: High-temperature Chip-Level Vacuum Packaging

In order to be commercially viable, LSI Micro Fuel Cell Chips must produce an attractive level of power output over the expected lifetime for a consumer product. Increasing the chip operating temperature improves the power output, but reduces the chip lifetime. The focus of Task 2 is to improve the vacuum sealing materials and processes to provide suitable lifetimes at higher operating temperatures.

2.1 Glass Compositional Changes

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.

A melting furnace capable of supporting development of higher temperature glasses has been installed and qualified at LSI. Several new glass formulations have been created using this new equipment. Analytical analyses of these glasses indicate that they crystallize more fully than current glasses, which should support higher reliability. Unfortunately due to delays in bringing the new high temperature furnace on-line, 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 full Fuel Cell Chip assemblies during the time frame of this project. New glass grinding equipment has been ordered which will allow paste manufacture and subsequent evaluation of the new glasses in prototype chips at a future date.

2.2 Barrier Layers

Chemical interaction between the sealing glass and the fuel cell die at elevated temperature has been investigated through the use of SEM EDS and is also believed to be a contributor to reduced seal life at higher temperatures. Several proprietary barrier layers were fabricated and evaluated for suitability in increasing seal lifetime at temperature.

Although some of the tested barrier layers showed promise in reducing the reaction between the sealing glass and the silicon fuel cell die, these materials proved difficult to integrate into the fuel cell die process flow and would require very substantial redesign of the MEMS chips to incorporate. However the investigation of barrier layers has lead to an improved understanding of the nature of the damaging chemical interactions, which in turn guided the positive work performed under Task 2.3 of this project.

Figure 3: Coupon burst strength with and without barrier layer

2.3 Die Structure and Process Improvements

In addition to issues associated with chemical reaction at high temperatures, adhesion loss between the sealing glass and the MEMS die can contribute to failure at temperature. By extending and incorporating changes to the stress and thickness of thin films currently incorporated in the fuel cell chips, a significant improvement in adhesion was observed in the fuel cell chip assemblies. A downside to these changes is that the optimized film is somewhat more sensitive to process variations, and the chip yield has decreased. Work on regaining historic chip yields is ongoing.

Experiments were also run aimed at reducing the chemical reactions between the thin film layer and the sealing glass. Insights gained from work performed on barrier layers under Task 2.2 of this project led to compositional changes in the thin films, resulting in improved operating temperatures for the fuel cell die. Although the target operating temperature of 800°C was not fully attained, a significant increase from 700°C to 750°C was realized.

Figure 4: Coupon burst strength as a function of layer thickness

2.4 Incorporation of Learning

Fuel cell chips were fabricated with both the improved electrodes developed under Task 1 and the operating temperature enhancements of Task 2. The result of these improvements was a new record in fuel cell chip output power that is a 2.5X increase over the power record at the start of this program. This represents a major step forward in the commercialization of the LSI Micro Fuel Cell Chip technology.

Figure 5: Normalized generator chip power

Task 2 Milestones

Target: Improve chip level vacuum packaging process to support operation at 800°C.

Achieved: The full target operating temperature of 800°C was not attained, but a significant increase from 700°C to 750°C was realized.

Target: Fabricate and test prototype SOFC system using the revised chip “build” that demonstrates improvement over current design.

Achieved: Fuel cell chips were fabricated and tested using the revisions developed under this program. The resulting chips provided a maximum output power that is a 2.5X increase over the power record at the start of this program.