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Low Temperature Co-fired Ceramics for Micro-Fluidics

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Abstract

The miniaturization of analytical instruments and packaging of novel sensors is an area that has attracted significant research interest and offers many opportunities for product commercialization. Low Temperature Co-fired Ceramics (LTCC) is a materials system composed of alumina and glass in an organic binder. LTCC is a good choice for sensor development because of the ease of incorporating features in the 'green' or unfired state such as electrical traces, fluidic pathways and passive electrical components. After a firing cycle, what remains is a robust, monolithic device with features embedded in the package. In order for LTCC to be a successful medium for small scale sensors or lab-in-package devices, fluid flow through channels and inlet/outlet ports must be perfected. Device inlet/outlet ports have been demonstrated by embedding sapphire tubes in LTCC, allowing external connections using compression fittings. Channels and cavities have been fabricated through the use of sacrificial carbon tapes and pastes. A field flow fractionation device used for separating or concentrating constituent components in a fluid and a multi-electrode electrochemical cell were fabricated with the techniques described in this paper.

Microfluidic Package Requirements

For LTCC to be successful as a materials system for the construction of lab-in-package devices, several challenges must be overcome. Fluidic or gaseous samples must be introduced and removed from the device. The sample must be moved through the device to the sensing location. Onboard reagents must be stored and metered. Electrical power and signals must be routed through the package as well as connected externally. Some devices may require visualization of the flow to monitor or measure reactions. All these requirements must coexist in the package.

LTCC was developed for the electronic packaging industry. The materials system has a number of conductive thick film pastes that allow the formation of electrical traces and planes, I/O contacts for edge connectors, solder contacts and wire bond contacts. Resistors, capacitors and inductors can also be created with co-fired pastes. Devices are constructed by machining, punching or laser drilling vias and channels on individual layers. The vias are filled with a conductive paste using a stencil and electrical features are screen printed onto the layers using the appropriate pastes. The individual layers are collated and laminated in a heated platen press, typically 20 minutes at 70°C and 20.7 MPa. The device is then fired in a furnace using the manufacturer's firing profile. The result is a monolithic device with embedded fluidic pathways and electrical circuitry. The

composition of the green tape results in a shrink rate of about 15% after firing.

Fabrication Techniques

Simple devices were constructed initially to develop the techniques for channel and cavity construction (Figure 1).

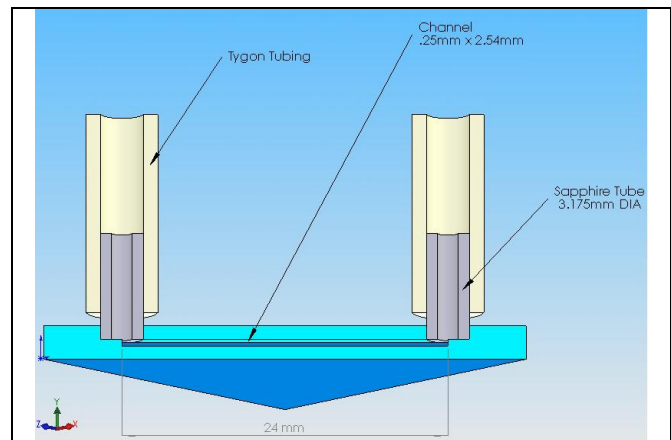


Figure 1 Cross section of simple channel device with embedded inlet and outlet ports.

Several options exist for the creation of a channel including the machined channel, the machined and filled channel and the embossed channel. A sacrificial carbon material is used both to fill machined channels and to form the channel in the embossed method [1, 2]. The desired quality and dimensions determine the technique used. The machined channel is the simplest to fabricate. Material is removed from a layer of green tape by milling or punching and the device is laminated and fired. One drawback of this technique is that during lamination, the channel can collapse.

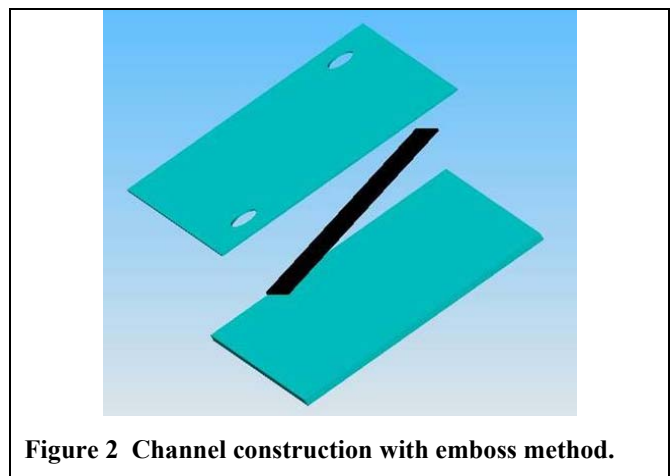


Figure 2 Channel construction with emboss method.

To prevent collapse, the channel can be filled with a sacrificial carbon material so that the channel is supported during the lamination step. The carbon material burns away at about 600°C. The duration of the burn out is a function of the quantity of carbon material, and the availability of oxygen in the furnace environment. The embossing method does not require machining of a channel and takes advantage of the green tape's ability to move during lamination. Sacrificial carbon material is placed between sheets of green tape in the desired channel configuration (Figure 2). The carbon can be applied as tape or paste. The layers are laminated and fired. The resulting channel has the geometry shown in Figure 3.

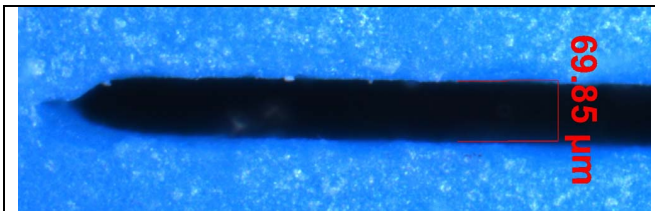


Figure 3 Optical micrograph of the cross section of a channel formed by the embossing method.

If the sidewall of the channel is required to be flat and orthogonal to the channel floor, the machined and filled method will provide the profile shown in Figure 4.



Figure 4 Optical micrograph of the cross section of a channel created by machining and filling with carbon.

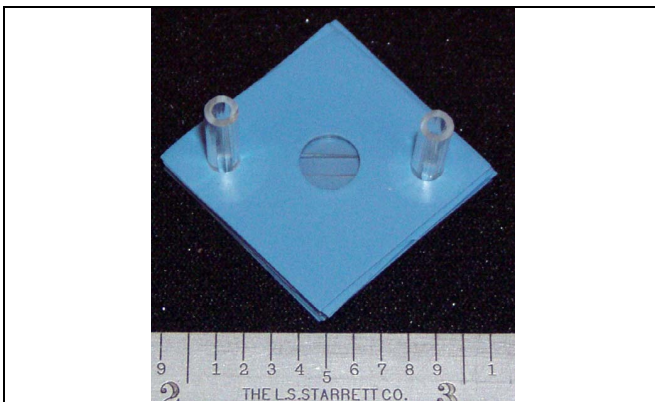


Figure 5 Simple channel with sapphire tubes fired into LTCC (inch scale).

In addition to internal channels, inlet and outlet ports must be provided. Several researchers [1, 3] have addressed the problem of introducing and removing samples from small

devices by brazing or soldering fluidic connections after firing the device. Another alternative is to incorporate the inlet and outlet ports during firing.

One of the components of the LTCC substrate material is Al_2O_3 which has melting point significantly higher than the firing temperature of LTCC, hence a sapphire tube is an ideal choice. To provide fluidic ports, a hole the same size as the tube is drilled into several layers of LTCC. During firing the shrinkage of the LTCC provides a tight seal around the sapphire tube. This method incorporates the natural shrinkage of the LTCC tape to capture sapphire tubes in the material. Successful devices (Figure 1) have been constructed and tested to 414 kPa. Testing is accomplished by connecting pressurized air to the device, immersing the device in water and observing bubbles that form from leaks. An optical micrograph of the interface between the sapphire tube and the fired LTCC substrate is shown in Figure 6.

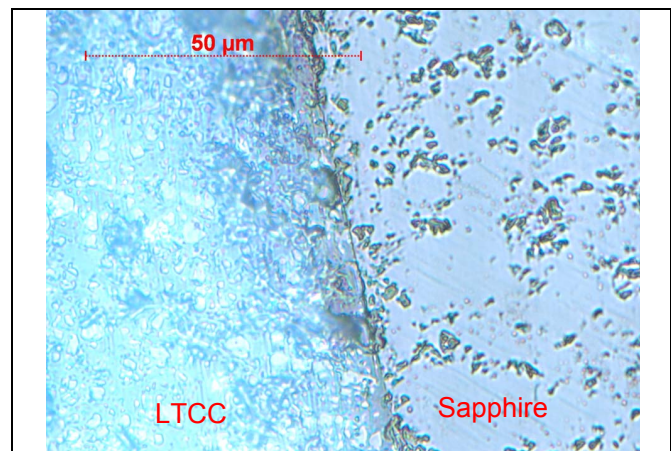


Figure 6 Optical micrograph of the LTCC sapphire tube interface.

In some fluidic devices, optical access is required to permit the use of lasers or photo-detectors. For example particles can be tagged with species that fluoresce. Sapphire lenses imbedded into LTCC have been demonstrated by Petersen et al [1]. Several prototypes using 6.35mm diameter lens were constructed using the three different methods illustrated in Figure 7.

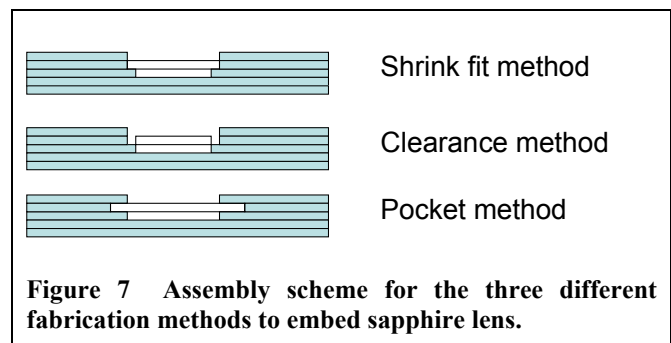


Figure 7 Assembly scheme for the three different fabrication methods to embed sapphire lens.

The shrink fit method involves drilling a 6.35mm hole in several layers of LTCC and inserting the lens in the hole. The device is then laminated and fired. The resulting device had excessive concavity. Because the lens does not contract with

firing, the upper and lower halves of the device shrink by different amounts. The clearance method increased the drilled hole size from 6.35mm to 7.14mm. The ~11% difference results in less impediment to shrinkage of the green tape by the sapphire lens resulting in less distortion to the fired part. Results yielded flatter devices but leakage occurred between the lens and the wall of the hole. The pocket method involves capturing the sapphire lens between layers of LTCC with smaller diameter holes (several sizes were attempted, 6.25mm and 6.05mm). The sapphire lens resides in a clearance hole of 7.14mm diameter. Pressure testing was accomplished by immersing the devices under water, applying pressurized air and observing the bubbles that form from the leaks. The clearance and pocket methods were more successful than the shrink fit method for low pressure (<7 kPa) seals, but high pressure seals are still under development.

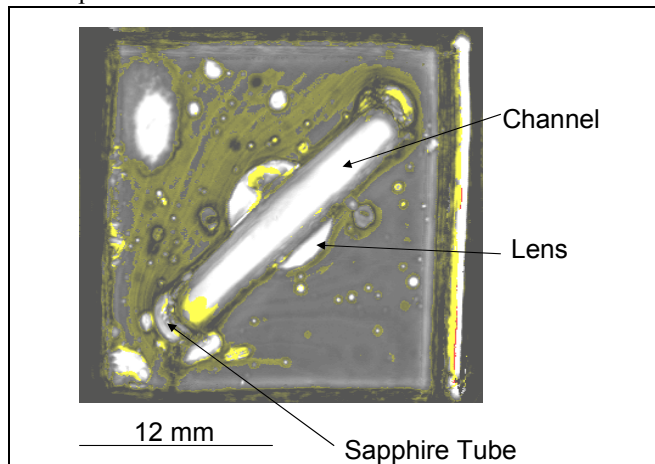


Figure 8 C-SAM results of channel device with sapphire tubes and lens (see device in Figure 5).

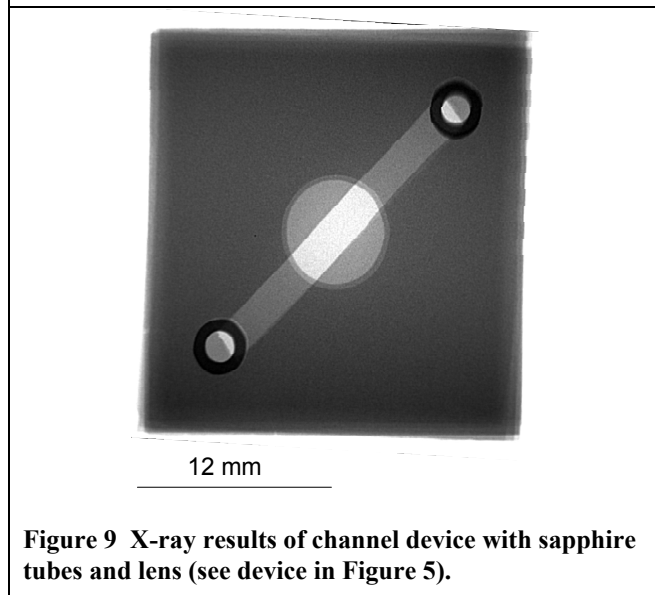


Figure 9 X-ray results of channel device with sapphire tubes and lens (see device in Figure 5).

Nondestructive Characterization

For a microfluidic package or sensor, nondestructive characterization of internal channels and cavities is critical to device development and manufacturing.

Several methods of characterization were explored. The most promising are Scanning Acoustic Microscopy and X-ray Tomography. Scanning Acoustic Microscopy (SAM) is a tool used extensively for detecting delamination in IC packaging by interrogating a part with an acoustic probe and measuring the change in density.

Applying the technique to the device in Figure 5 provides the results seen in Figure 8. While the channel and lens are distinguishable with some detail, the sapphire tubes are less defined. Because the technique is measuring changes in density with acoustic waves, metallic pastes affect the ability to see channel detail.

In the method of X-ray tomography reported by Santiago-Aviles et al [2], samples are bombarded with X-ray radiation. Materials absorb the energy at different rates resulting in images appearing on the detector (or film) behind the sample. The image in Figure 9 was obtained by applying the X-ray process to the device in Figure 5 and demonstrates the capability to distinguish the different components and features from one another. A comparison between Figure 8 and Figure 9 (same device in both cases) shows how crisp and clear the X-ray image is compared to the C-SAM image. Both techniques can be of use in microfluidic packaging development.

Field Flow Fractionation Device

Field Flow Fractionation (FFF) is a method of separating colloidal particles such as liposomes, proteins, or other particulates that are suspended in a fluid [4]. By applying a thermal gradient or an electric field across a channel with a high aspect ratio (width to height), particles are driven to the top (or bottom) wall where they are subjected to a lower average velocity than particles located further from the wall. Consequently, particles move at different velocities depending on the strength of their interaction with the field, and concentrate into bands as they move toward the channel outlet as seen in Figure 10.

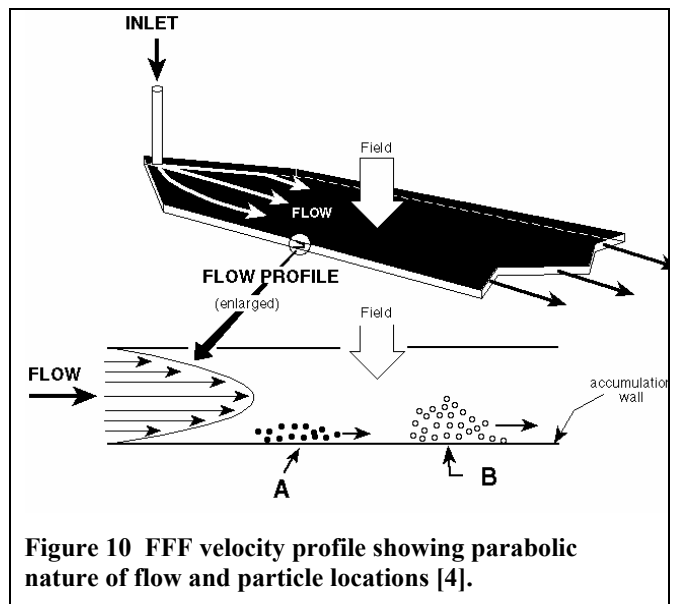


Figure 10 FFF velocity profile showing parabolic nature of flow and particle locations [4].

A small scale FFF eliminates the problems associated with the voltage potential required for generating a uniform field

across the large scale FFF. Channel heights in the 100's of μm resulted in voltage potentials that were detrimental to some of the samples. Because FFF is a separation or concentration technique, it was desirable to construct it out of LTCC so it could be incorporated into sensing devices. The initial version of the FFF was constructed with an estimated channel height of $42\mu\text{m}$, a width of 4.35mm and length of 93.8mm as seen in Figure 11. The silver pads on top of the device are connected by vias to electrodes that surround the channel and provide the means to apply an electric field across the channel. The properties of LTCC easily allow other techniques to be applied such as thermal gradients or magnetic fields.

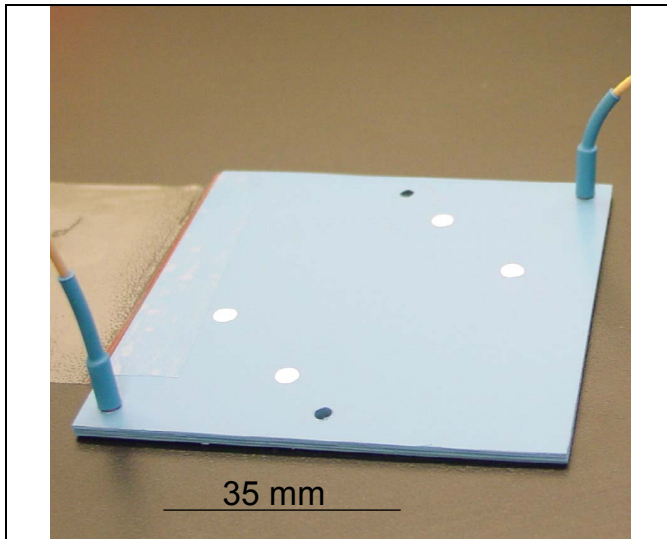


Figure 11 Field Flow Fractionation device in LTCC with sapphire tube inlet/outlet ports under flow test.

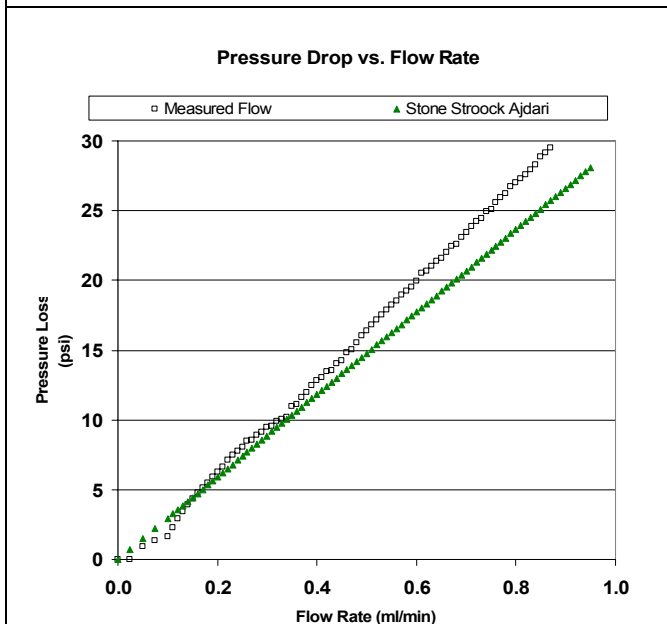


Figure 12 Theoretical and experimental pressure drop through the FFF device in Figure 10.

Preliminary testing was conducted to evaluate pressure and flow rates through the device before attempting separation. The evaluation was conducted using toluene as the fluid. The solution was pumped through a Waters model 590 HPLC pump at various flow rates. Flow rates from the instrument were verified with a Class A Burette to have less than 1% error. A stainless steel back pressure regulator assembly rated at 500 psi was utilized in-line just after the pump to dampen pulsing effects. An Alltech® On-Line Degassing System™ was used on the intake of the pump while the discharge side had the pressure gauge and an inline filter assembly.

Figure 12 shows the pressure loss versus flow rate for the measured flow and the theoretical flow as predicted by the model developed by Stone et al [5]. The model is derived from classical Stokes flow with a no-slip boundary condition. The strong correlation shown indicates a well formed channel.

This device is currently undergoing functional testing where a slug of sample is introduced into the solvent flow stream through a three way valve assembly.

Electrochemical Cell

Electrochemical techniques, such as Electrochemical Impedance spectroscopy (EIS) and Cyclic Voltammetry (CV), are commonly used to measure changes at electrode surfaces. Because electrochemical techniques measure the potential of one electrode relative to another, at least two electrodes are required in an electrochemical cell. A typical 2-electrode set-up consists of a Working Electrode (WE) and a Reference Electrode (RE). A RE should exhibit a constant potential over the potential range under study (i.e. the RE potential does not change with changes in potential in the system). Therefore, adjusting the potential across the WE and RE will be compensated by a change in potential at the WE/solution interface.

An EC Cell device was designed (Figure 13) using a 2 electrode set-up in which both the WE and RE were constructed of fired gold paste. The WE consists of a 4×4 array of $500\mu\text{m}$ diameter gold electrodes on the floor of a micro-cavity with a $4\text{mm} \times 4\text{mm}$ gold working electrode printed on the ceiling. Sapphire inlet/outlet ports provide sample access to the cavity as well as access for a reference

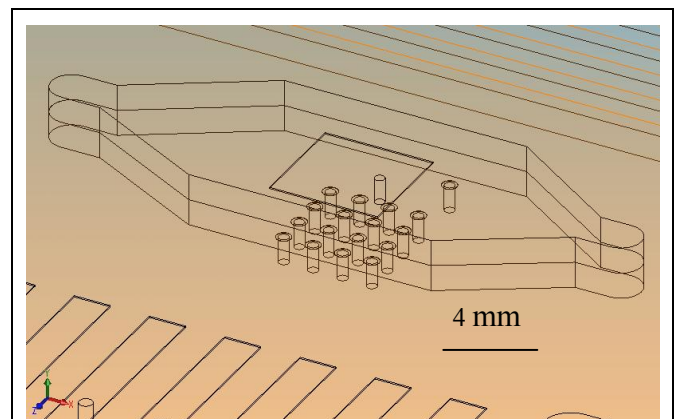
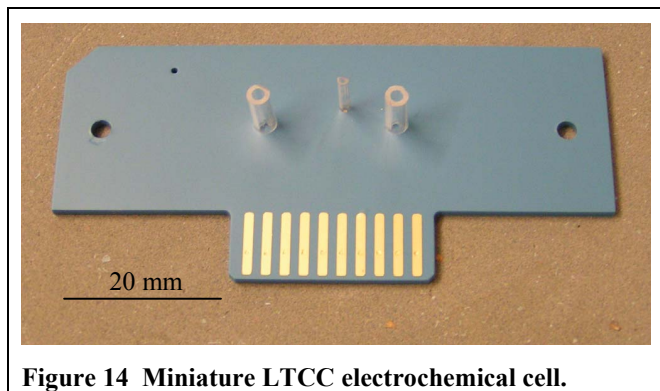
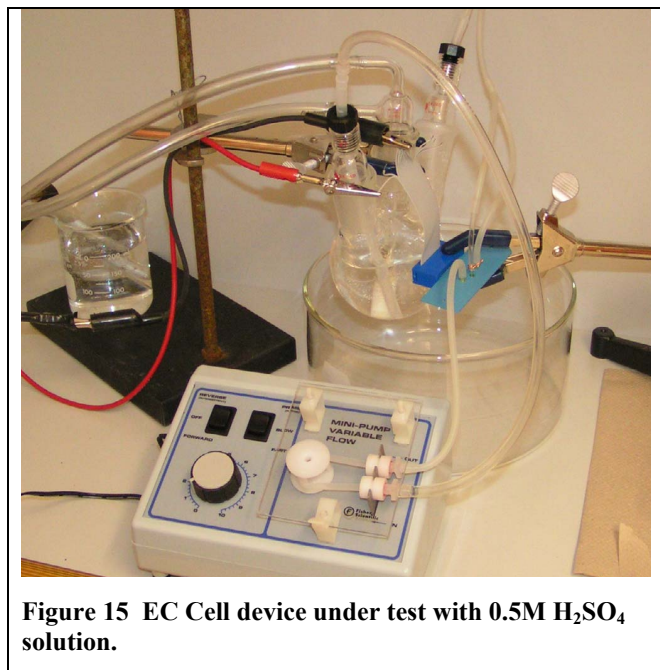


Figure 13 Internal view of EC Cell device showing cavity geometry, working electrodes and counter electrode.

electrode. The RE surface is orders of magnitude larger than the WE. Due to the large surface area of the RE, the rate-limiting reactions occur at the WE/solution interface. In addition, the potential change at the RE/solution interface is considered to be negligible. Because a 2-electrode set-up can only measure the potential difference between the two electrodes, all measurements must be made versus a measured open circuit potential (E_{oc}).



Several electrochemical cells (Figure 14) were constructed from LTCC. The ability to combine both fluidic and electric networks in the same package makes LTCC a great choice for a miniature EC Cell. The miniature EC Cell devices were tested using EIS and CV. Preliminary results are consistent with others using conventional laboratory glass apparatus and gold working electrodes of 6 mm diameter [6, 7] and microelectrodes of 100 μ m diameter [8].



The device under test is shown in Figure 15 connected to a closed system that was purged with argon for several hours. A peristaltic pump circulated the 0.5M H_2SO_4 solution at a low flow rate throughout the experiments. In the experiments, the electrode was cleaned by holding at -1V versus E_{oc} for 200 seconds. The open circuit potential was

measured until it stabilized, in this case in excess of 1 hour, and the CV or EIS experiment was conducted. Stability was observed typically within 3 cycles in the CV experiments.

The CV results in Figure 16 show the double hump (about 0.8 V) on the positive sweep indicating the formation of oxides on the gold surface followed by a sharp increase in current due to oxygen evolution. The negative sweep shows the reduction (about 0.9 V) of the surface oxide with a secondary hump that differs from the results of others [6, 7]. A possible explanation for this difference is the rough surface of the gold electrodes in this cell may contain many pores. Micro-pores and micro-crevices can affect the reduction/oxidation response.

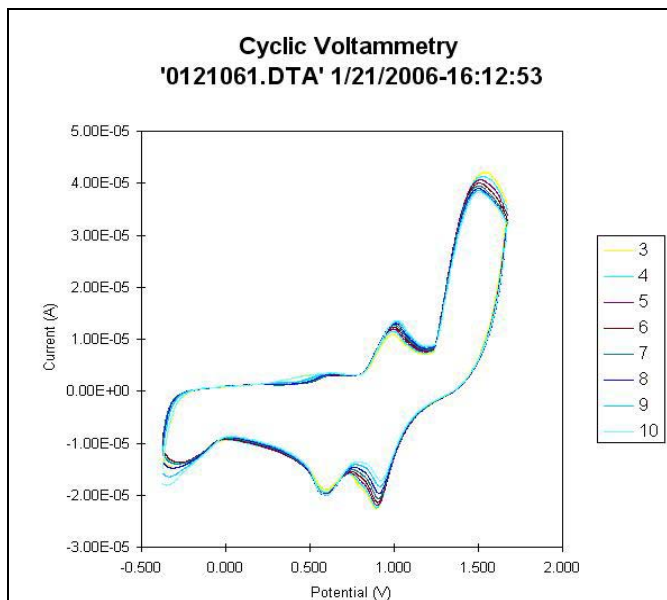


Figure 16 Cyclic Voltammogram of gold working electrode, gold counter electrode in 0.5M H_2SO_4 solution versus open circuit potential.

For more accurate potential measurement, a 3- electrode set-up should be used. A 3-electrode set-up consists of a WE, RE and a Counter Electrode (CE). Potential is controlled by allowing current to pass between the WE and the CE. By placing the RE near the surface of the WE, the potential of the WE can be controlled relative to the RE. Standard RE's, with known potentials, are generally used and very little, or no, current passes through the RE. Because no current passes through the RE, it does not become polarized and its potential remains constant over a range of potentials.

The EC Cell device will be used as a detector with a gradient electrode array. Electrodes are functionalized with linking chemistry to which specific receptors are attached. When target species in the sample are encountered and captured by the receptor, the double layer capacitance of the electrode changes. Through variation of the properties of the electrodes in both directions of the array, combinatorial analysis provides high sensitivity and selectivity. Sullivan et. al [9] constructed a similar device on silicon using gold electrodes and various lengths of alkanethiols.

Conclusions

Several LTCC devices have been constructed and tested as building blocks for lab-in-package devices. The FFF and EC Cell devices could ultimately be combined in the same package such that the FFF would act as a concentrator for an EC Cell. Various techniques have been presented that show different methods of constructing the fundamental features required in fluidic packaging. Final inspection techniques were also presented.

Acknowledgments

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