

Using High Volume Electronics Manufacturing Technology to Develop a High Volume Fuel Cell Manufacturing Process

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During the last several years there has been and continues to be an enormous investment by both governments and industry in the development and manufacture of fuel cells. The United States, Japan, and European Union have invested billions of dollars on research and development. Major Universities including MIT, Northwestern, and others have significant fuel cell research projects. Many large multi-national corporations including all of the major automotive suppliers are investing billions on fuel cell technology. Fuel Cells are being viewed as an environmentally friendly infinitely renewable fuel source that will reduce the United States and other industrialized nations dependence on foreign oil.

Both large fixed portable fuel cells and portable fuel cells are being developed. Large fixed fuel cells have been available for some time and are used to power industrial and commercial facilities. Some fixed fuel cells are now powering private homes in some areas. The goal is to have “thousands” of fuel cell automobiles on the road in the next few years and the majority of automobiles powered by fuel cells within 10 years. Portable fuel cells are being developed as battery replacements for cell phones and other common battery powered items.

One of the major issues with fuel cell acceptance is the cost of the energy produced by a fuel cell versus the cost of energy produced by the competing energy sources. There are several technical challenges to developing cost effective fuel cells.

One of the key areas to reduce fuel cell cost is the manufacturing cost.

Once solutions to the technical challenges are discovered and the cost reduced, high volume fuel cell manufacturing will be a reality. Can and if so how can high volume electronics manufacturing technology be used to develop and implement high volume fuel cell manufacturing?

This paper will discuss the use of high volume electronic manufacturing technology, specifically screen printing and mass curing, in high volume fuel cell manufacturing.

What is A Fuel Cell?

A fuel cell is an energy converter. It converts the chemical energy of the reaction between a fuel and oxygen directly into electrical energy, through at least two electromechanical processes.

Fuel and oxygen do not get into a direct contact. Oxidation of the fuel and reduction of oxygen takes place at two physically separate places called electrodes. An example of such a cell, using hydrogen as the fuel, is shown in Figure 1. A generic cell example is shown in Figure 2.

The reaction of the fuel and oxygen generate electricity with water (Figure 1) or water and other exhaust materials (Figure 2) as by-products. A typical example is shown in Figure 3.

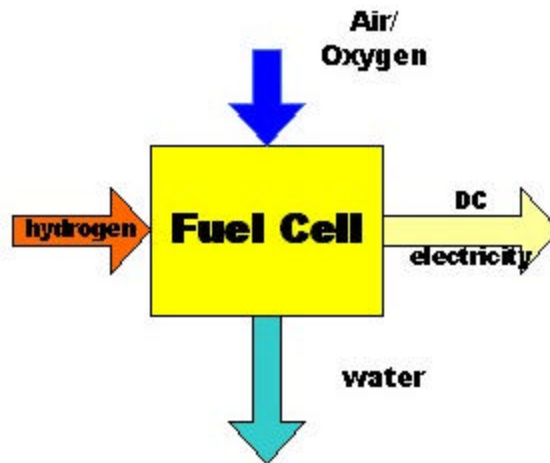


Figure 1 – Simplified Hydrogen Fuel Cell

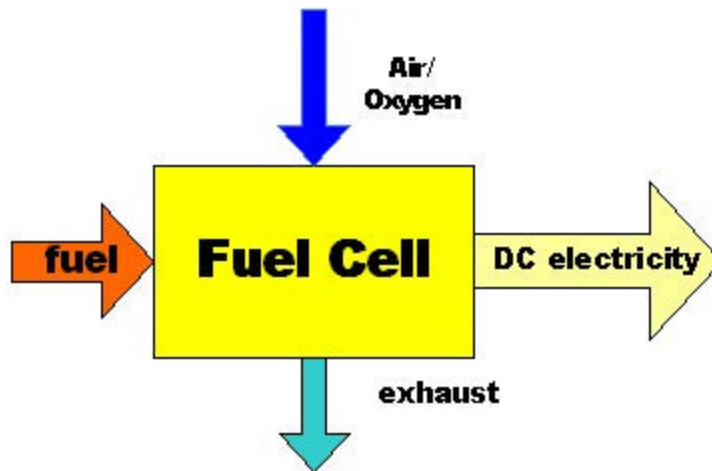


Figure 2 – Generic Fuel Cell

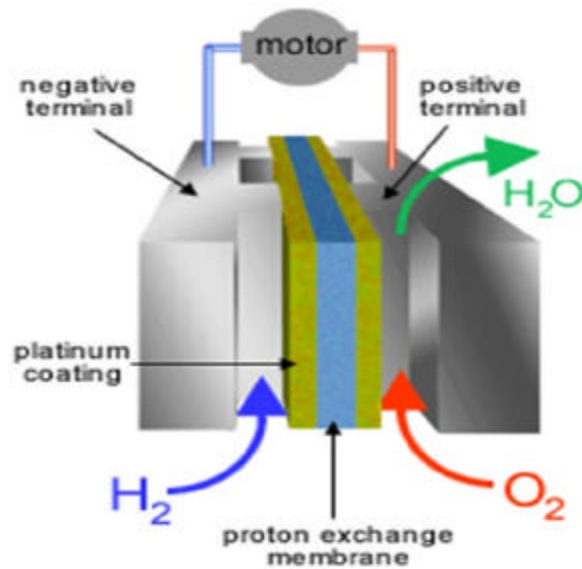


Figure 3 – Fuel Cell: Simplified Operation

A complete block diagram of a fuel cell system is shown in Figure 4.

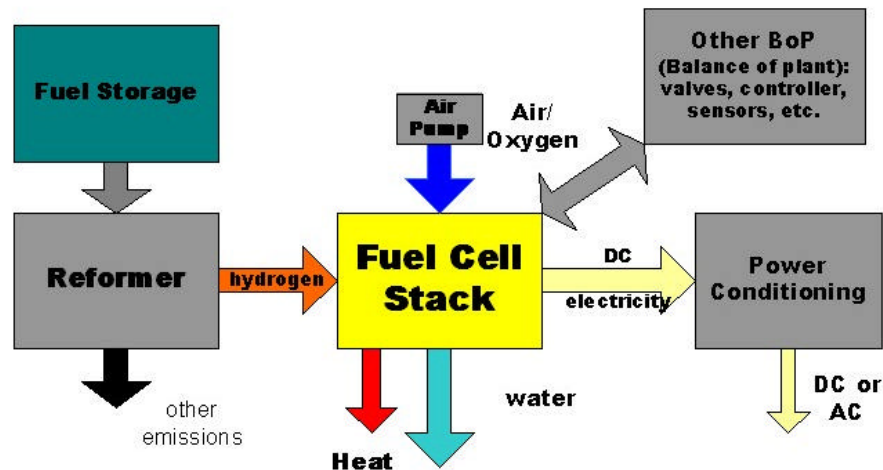


Figure 4 - Components of a Fuel Cell System

Fuels a Fuel Cell can Utilize

A fuel cell can utilize anything that when combined with oxygen yields energy.

However, a good fuel should:

- Be abundant, inexpensive, and safe
- Easy to undergo the electromechanical oxidation = release its electron(s)
- Produce non toxic emission

In practice there are few fuels that meet all the criteria. It comes down to three fuels:

- Hydrogen
 - Preferred fuel, due to relatively low thermodynamic and electromechanical losses (quick and easy reaction)
- Light Hydrocarbons
 - Natural gas/methane/LPG
- Lower Alcohols
 - Methanol/Ethanol

Hydrogen is thermodynamically the ideal fuel.

- High Efficiency
- High Energy Content
- Benign Emissions: Water
- Higher power outputs/current densities

Table 1 compares the properties of some of the fuel choices with hydrogen.

Table 1 - Hydrogen Properties Comparison

	Hydrogen	Natural Gas	Gasoline
Color/Toxicity	None / no	None / no	Yes / yes
Odor	Odorless	Mercaptan	Yes
Specific Gravity	0.07	0.424	Liquid (>1)
Emissions	None	CO ₂ / NO _x	CO ₂ / NO _x
Diffusion Coefficient – cm²/s	0.61	0.15	Liquid
Flammability Range (in air)	4-75%	5.3 – 15%	1.4 – 7.6%
Ignition Energy (mJ)	0.02		0.20
Heat Value (kJ/kg)	119,972	50,020	42,847
Energy Density (MJ/Nm³)	10.78	35.88	104.4

The Five Basic Chemistries

There are five basic fuel cell chemistries for fuel cells: Proton Exchange Membrane FC or PEMFC, Alkaline FC or AFC, Phosphoric Acid FC or PAFC, Molten Carbonate FC or MCFC and Solid-Oxide FC or SOFC.

Not all of these chemistries are equivalent.

Proton Exchange Membrane FC (PEMFC) Pros and Cons:

- Solid electrolyte = can operate in any orientation
- Low operational temperature = can start quickly, low energy (quality of heat)
- Expensive catalyst (10 \$/kW)
- Widest range of power outputs, few watts to 100s kW
- Sensitive to CO poisoning, require additional fuel treatment

Alkaline FC (AFC) Pros and Cons:

- Low to medium operational temperature
- Inexpensive catalysts
- Alkaline electrolyte – OH⁻ ionic transport
- High power densities
- Killer: CO₂, carbonates precipitate inside = not good for terrestrial applications, but still fine for H₂/O₂ systems

Phosphoric Acid FC Pros and Cons:

- Electrolyte: 100% phosphoric acid
- Similarities to PEM: expensive catalyst, CO sensitive, H⁺ ion transport
- Good for stationary power generation
- The only truly commercially available FC chemistry (UTC's PS25), though still very expensive (\$400/kW)
- Life is an issue - for power plants is typically required 40,000 hrs

Molten Carbonate FC Pros and Cons:

- Capable of 'internal reforming'
- Unlike other FC, MCFC consumes CO₂, plus not sensitive to CO,
- Cathodes tend to dissolve in molten carbonate
- For stationary generation only
- Stack degradation a challenge
- Molten electrolyte requires recycling and management

Solid Oxide FC Pros and Cons:

- Completely solid-state device = can operate in any orientation
- Suitable for CHP (combined heat and power) generation, with very high overall efficiency
- Tubular and planar designs
- Design and operational difficulties associated with operating at high temperature (1000 C)

A comparison of the differences of these chemistries is shown in Table 2.

Table 2 - Some Practical Differences

	Typical power output	Temperature range, C	Catalyst/ Active ion	Technical challenges	Applications
PEM	1W-100kW	50-200	Pt, Pt/Pd H ⁺	CO-poisoning Expensive catalysts	Various:
Alk FC	1- 5 kW	80-200	Raney Ni, NiO, Pt/Pd OH ⁻	CO ₂ poisoning	Space missions
PAFC	200 kW	220	Pt, Pt alloys H ⁺	Life	Stationary generations , DG
MCFC	Up to MW	650	Nickel, NiO CO ₃ ⁻	Corrosive electrolyte	Stationary generations , DG
SOFC	1kW - several MW	500-1000	Zirconia nickel O ²⁻	High temperatures	Various stationary generators and engines

PEM and SOFC are the most promising chemistries. PEM and SOFC are the best candidates for mass production that requires the use of less expensive materials and demands improved manufacturing technologies.

PEM Fuel Cells

The PEM Fuel Cell Stack Engine or the “Core” consists of Membrane Electrode Assembly (MEA) and a Bipolar Plate:

- Membrane Electrode Assembly (MEA)
 - A five layer membrane built around the electrolyte membrane
 - Electrodes are sprayed, painted or otherwise built directly onto the electrolyte – “catalyst coated membrane”
 - Gas diffusion medium is then added
- Bipolar Plate (BBP)
 - Nonporous structure that provides electronic conduction, separates reactant gases, supplies anode with the fuel and cathode with the oxidant (hence “bipolar”)

The three layers in the middle are the heart of the fuel cell system and are called Catalyst Coated Membrane (CCM).

A diagram of this type of fuel cell structure is shown in Figure 5. An example of an operating 770 watt “stacked” fuel cell is shown in Figure 6. Details of the “stack” design are shown in Figure 7.

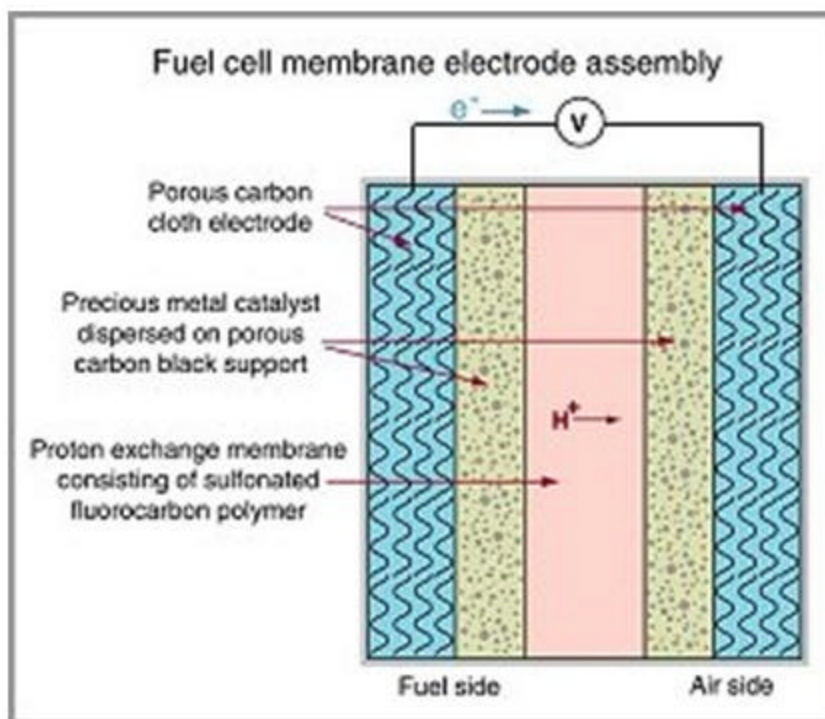


Figure 5 – Fuel Cell Layout



Figure 6 - Fuel Cell Stack (PEM, 700W, 65 Cells)

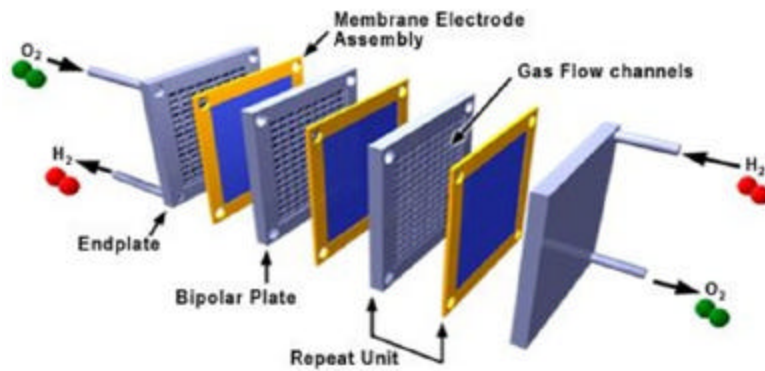


Figure 7 - Assembling the Stack

Solid Oxide Fuel Cell (SOFC) Electrolyte

In a SOFC the electrolyte is composed of oxides of zirconium and yttrium and oxide mixtures known as perovskites. The key feature of this type of structure is its ability to become an ionic conductor at elevated temperatures (>800C), for O^{2-} ions. These materials can be made very thin i.e. 25-50 nm. The main process used for creating these structures is “Electrochemical Vapor Deposition” (comparable to PVD - physical vapor deposition technology in semiconductor fabrication). Novel systems may use a mix of Lanthanum, Strontium, Gallium, and Magnesium Oxides, i.e. LaSrGaMgO or LSGM.

The SOFC electrodes, the anode and cathode, differ in structure. The differences are listed below.

- Anode:
 - Intimate mixtures of metals (nickel) and ceramics, a.k.a. “cermet”
 - Thermal expansion compatibility
 - High porosity (20-40%) to ease mass transfer
- Cathode: a classical semiconductor at room temperature
 - Most commonly used cathode material is lanthanum manganite ($LaMnO_3$), a p-type perovskite. Typically, it is doped with rare earth elements (e.g. Sr, Ce, Pr) to enhance its conductivity
 - Two designs: tubular and planar

A diagram of the structure is shown in Figure 8.

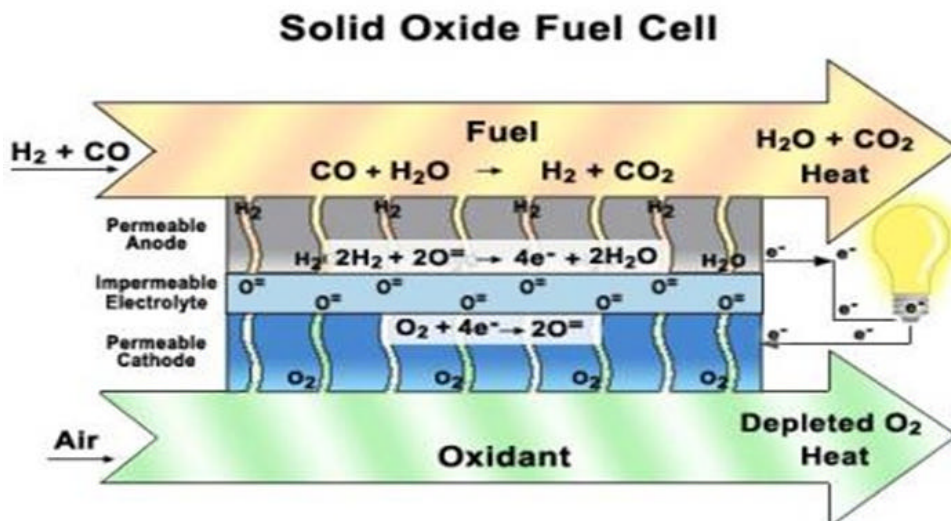


Figure 8 – The Solid Oxide Fuel Cell Structure

Fuel Cell Markets

There are four segments that the various types of fuel cells fit into.

- Stationary e.g. heat, electricity home/commercial
- Transportation, e.g. Automobile, truck, aircraft
- Portable, e.g. transportable power RV, camping, military, etc.
- Micro, e.g. battery replacement for cellular, PDA, Laptops, etc.

A comparison of the markets and power needs is show schematically in Figure 9.



Figure 9 – Fuel Cell Markets by Power Application and Sales

Fuel Cell Advantages and Disadvantages

It is important to understand how fuel cells relate to each of the other types of energy converters such as internal combustion engines, electrical generators, storage batteries, solar systems, and gas turbines.

There are at least four advantages to fuel cells over existing power sources: efficiency, simplicity, benign emissions, and silent operation. Fuel cells are more efficient (40-75%) than internal combustion engines (20%). Small systems can be as efficient as large ones. With no moving parts fuel cells are reliable and long lasting. When Hydrogen is used the emission is pure water. Silent operation is especially important in both local power generation and portable/special applications.

The major disadvantage of fuel cells is the energy cost. The existing energy sources such, as energy supplied by the power grid is much less expensive.

Additional disadvantages include

- Complicated fuel management
- Immature technology, capricious behavior
- Unreliability
- Short durability
- Low/high temperature behavior
- Well-entrenched and mature competing technologies, e.g. internal combustion, gas turbines, and batteries.

Still there is great potential for fuel cells with many active players in that market as is shown in Figures 10 and 11 and Table 3.

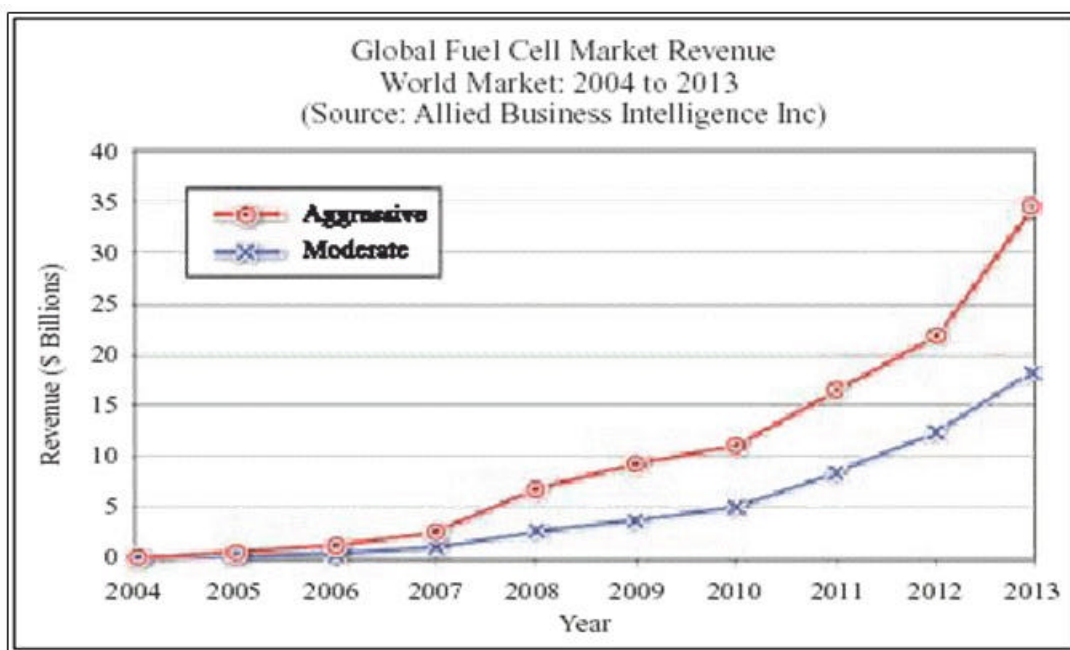


Figure 10 – Global Market Predictions

Global PFC Production Forecast, 2004-2011
(Source: Allied Business Intelligence, Inc.)

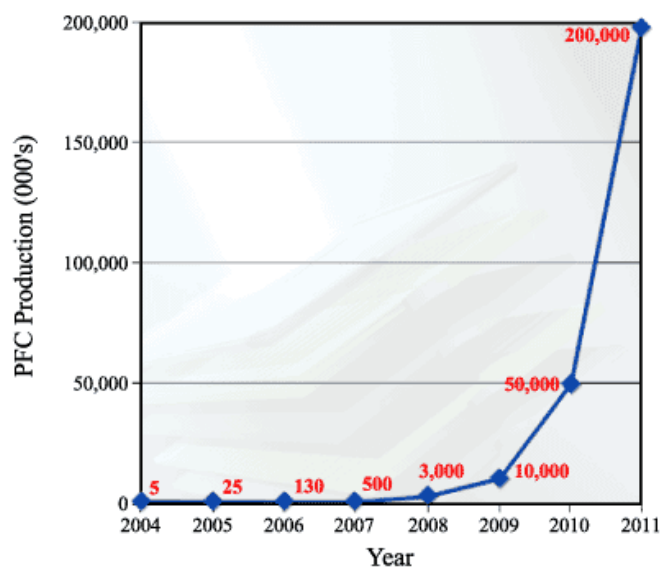


Figure 11 – Production Forecast

Table 3 – The Main Players in Fuel Cells

<i>Fuel cell type</i>	<i>Company</i>	<i>Location</i>
Alkaline	International Fuel Cells	USA
	Zevco	Belgium/UK
Solid Polymer	Advanced Power Sources	UK
	Avista Labs	USA
	Ballard	Canada
	DeNora	Italy
	Energy Partners	USA
	Fuji Electric	Japan
	H Power	USA
	Mitsubishi Electric	Japan
	Plug Power	USA
	Siemens	Germany
	Toyota	Japan
Phosphoric Acid	ONSI	USA
	Toshiba	Japan
Molten Carbonate	Energy Research Corporation	USA
	MC-Power	USA
	Motoren und Turbinen Union	Germany
	Ishikawajima-Harima Heavy Industries	Japan
Solid Oxide	Allied Signal	USA
	Ceramic Fuel Cells	Australia
	Mitsubishi Heavy Industries	Japan
	Rolls-Royce	UK
	Siemens-Westinghouse	Germany/USA
	Sulzer Hexis	Switzerland

Additional players in the fuel cell market include Delphi Automotive, Daimler Chrysler, Ford, GM, Motorola, Nuvera, General Electric and J Matthey.

Industry References to Fuel Cell Manufacturing

Fuel cells can be manufactured using a variety of processes. Examples from Motorola and Cummins are shown in Figures 12 and 13. A comparison of several companies' approaches is shown in Figures 14 and 15.

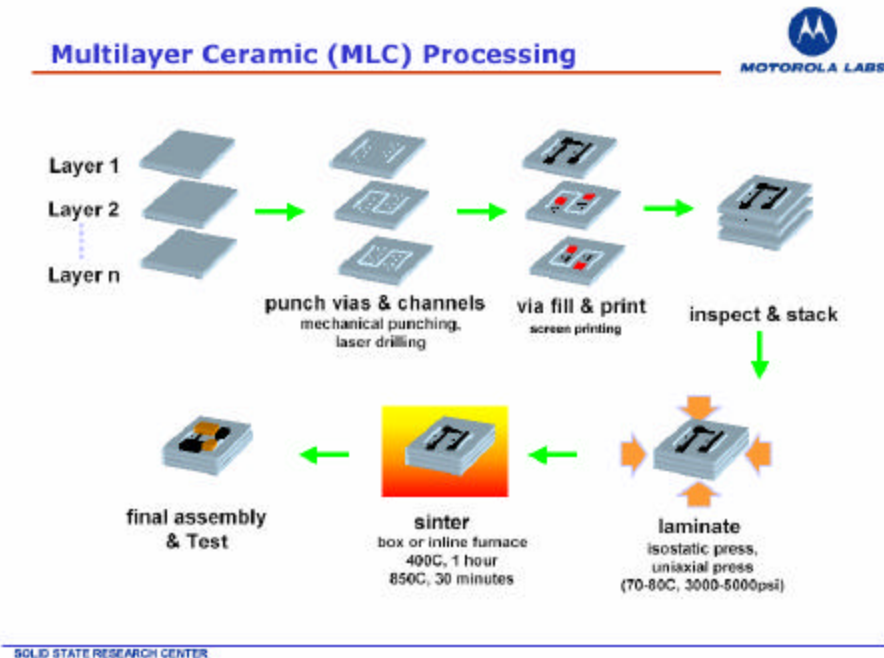


Figure 12 – Motorola Process

Advantages of MTI-SOFCo Technology

- Eliminates metal interconnects and ceramic-metal seals (major sources for stack degradation)
- Less susceptible to thermal cycling problems
 - Good CTE match between cell and multi-layer ceramic interconnect
- Reduced contact resistance between cells and interconnects
- Requires fewer sintering steps
- Low-cost, high-volume manufacturing infrastructure established

Figure 13 – Cummins Process

Different Approaches!

<i>Team</i>	<i>Design</i>	<i>Manufacturing</i>
Cummins-SOFCo	<ul style="list-style-type: none"> • Electrolyte supported • 850 C • Thermally matched materials • Seal-less stack 	<ul style="list-style-type: none"> • Tape casting • Screen printing • Co-sintering
Delphi-Battelle	<ul style="list-style-type: none"> • Anode supported • 750 C • Ultra compact • Rapid transient capability 	<ul style="list-style-type: none"> • Tape casting • Screen printing • 2-stage sintering
General Electric Company	<ul style="list-style-type: none"> • Anode supported • 750 C • Hybrid compatible • Internal reforming 	<ul style="list-style-type: none"> • Tape calendaring • 2-stage sintering
Siemens Westinghouse	<ul style="list-style-type: none"> • Cathode supported • 800 C • Redesigned tubular • Seal-less stack 	<ul style="list-style-type: none"> • Stack extrusion • Plasma spray



WPG, CPPO-DWC 43002

Figure 14 – Comparison of Fuel Cell Design Strategies

Two New Different Approaches!

<i>Team</i>	<i>Design</i>	<i>Manufacturing</i>
Acumentrics Corporation	<ul style="list-style-type: none"> • Anode supported microtube • 750 C • Thermally matched materials • Robust & rapid start-up 	<ul style="list-style-type: none"> • Extrusion • Dip processing • Spray deposition
FuelCell Energy, Inc.	<ul style="list-style-type: none"> • Anode supported • < 700 C • Low cost metals 	<ul style="list-style-type: none"> • Tape casting • Screen printing • Co-sintering • Electrostatic deposition

Figure 15 – Comparison of Fuel Cell Design Strategies

A New Strategy

One approach that several of the companies involved in fuel cell manufacture have tried is screen-printing. Screen printing has long been a staple of electronics assemble and as such lends itself to high volume, robust manufacturing. An example of such a process is shown in Figure 16 for SOFCs.

Industry Consensus

There is an industry consensus that screen printing is a viable, low cost manufacturing solution for flat type SOFC membranes. Indeed, it should be the lowest cost in certain models. In addition, it is a well understood process that is widely available. In some cases screen printing is displacing spray processing.

It would seem that screen printing can enable a very low manufacturing cost model (multilayer-flat cells) by reducing co-cure steps when compared to spray process.

Ultimately, the decision to deploy screen printing vs. spray is driven by fuel cell power density/film thickness (stack depth/current/FC outline) and configuration (flat vs. tubular).

SOFCs Fabricated by Screen-Printing

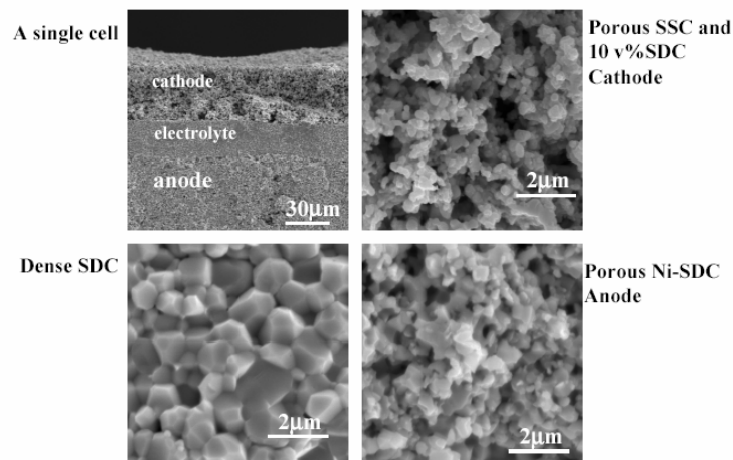


Figure 15 – Fuel Cell Assembly Using Screen Printing

Fuel Cell Manufacturing

Based on the dramatic increase in the predicated fuel cell system volumes over the next ten years it will be necessary to use high volume manufacturing methods to satisfy this predicted demand. Currently most fuel cell manufacturing is done with low volume methods using low volume batch type equipment. Fuel cell manufacturers are predicting requirements for several second substrate cycle times over the next five years. The SMT high volume manufacturing technologies can support the fuel cell manufacturing cycle time goals.

Another major factor in achieving the high volume demand for fuel cells is to reduce product cost. Currently the major disadvantage of fuel cells is their costs. There are several factors that contribute to the current fuel cell cost. One of them is the manufacturing cost. Fuel cell manufacturers must reduce the cost of their manufacturing processes to support the cost goals.

One of the high volume fuel cell technologies will be Flat Type Solid Oxide Fuel Cells (SOFC). This technology uses flat ceramic type material substrates. The substrates then have a sequential variety of conductive inks applied to both the bottom and the top. Between each application of the conductive ink the ink must be cured in an oven. Today this process consists of batch type screen printers to apply the layers of conductive inks and batch type ovens to cure the printed conductive inks. Each subset is printed and manually removed from the batch screen printer and then manually placed in a batch oven for curing. The cured substrate is then manually removed from the oven and manually placed back into the batch screen printer. This process is repeated until all the conductive ink layers are applied and cured. There are a number of ceramic substrates in each completed fuel cell system. A typical printer is shown in Figure 16.



Figure 16 - Batch Type Screen Printer used in Fuel Cell Manufacturing Today

The final step in the manufacture of the individual ceramic substrate is high temperature (500-1400+ deg C) curing. This is the one process step that is not a high volume SMT manufacturing process. There are a number of existing suppliers of these furnaces.

The electronic manufacturing industry has developed high-speed in-line screen printing and curing/reflow processes. These high volume-manufacturing processes and equipment can be used in the high volume manufacturing of some types of fuel cell systems.

The screen-printing process involves printing conductive inks using a screen. The thickness of each conductive ink layer is too thin and the required deposition is too large to consider stencils for this application. The conductive inks used today can be commercially available or a proprietary material from a particular fuel cell manufacturer. Today's in line high-speed vision alignment screen printers are ideal for this application.

The curing process involves transporting flat substrates thru an oven. The existing in line curing/reflow ovens used in the SMT are ideal for this application.

High Volume Fuel Cell Manufacturing Process Development

There are several factors that need to be learned and understood in the development of the high volume fuel cell manufacturing process.

1. The first step is to understand the tolerances of the printed conductive inks.
 - What is the upper and lower specification limit of the printed inks thickness?
 - What is the precision requirement of the printed conductive ink pattern?
 - What is the precision of each conductive ink layer printed over the previous layer?
 - What is the pot life of the conductive ink?
 - What is the fineness of grind of the solids in the conductive ink?
2. Design the screen.
 - Can we design and fabricate a screen that will satisfy the precision and tolerance specifications?
 - How large is the substrate in comparison to the screen size maintaining the 150% rule for freeboard area?

3. Perform formal process development studies and experiments.
 - How fast can we print these materials?
 - How fast can we transport the substrates into and out of the printers?
 - What substrates support is required during the printing process?
 - How well can the printer align these substrates with the screen?
 - How long will a screen last before it stretches beyond the dimensional requirements of the substrate?
 - What are the process control limits for deposition thickness, width, length, etc.?
 - What is the usable life of this material once it is on the screen?
 - Can this material be printed using an “enclosed print head”?
 - Is tooling required to process multiple substrates in order to achieve the cycle time goal?
4. Develop the high volume curing process
 - The primary issue will be to determine what combination of oven capacity and tooling will be required to achieve the cycle time goal. There are several alternatives such as using multiple ovens, ovens with two or more tracks (conveyors), tooling the substrates so they can be transported on an edge to increase oven capacity, etc. Once the exact sizes of the substrates are defined we can perform a capacity study and model several alternatives.

Conclusion

There is a great deal to learn in the development of high volume fuel cell manufacturing. However, the high volume in line screen printing process and curing process that is used today in the high volume SMT electronic Industry is ideally suited to support the fuel cell manufacturing cycle time requirements.

A number of companies are starting detailed high volume full cell process development projects that will utilize the equipment, knowledge, and experience of the high volume SMT electronics manufacturing industry.