Evaluation of Micro Solid Oxide Fuel Cell Technology

by

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Submitted to the Department of Materials Science and Engineering
In Partial Fulfillment of the Requirements for the Degree of
Master of Engineering in Materials Science

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ABSTRACT

Micro solid oxide fuel cells are one type of fuel cell being researched for use in portable electronic devices or applications requiring portable power. This emerging technology combines fuel cell technology with microfabrication technology to achieve a micro sized fuel cell on a small silicon die. The potential exists for outperforming standard battery technology by an order of magnitude.

A review of micro solid oxide fuel cell technology and its main technical challenges is done. Critical evaluation of the energy density of the micro solid oxide fuel cell based on assumptions of efficiency and packaging is made. Discussion of possible use models of micro solid oxide fuel cells and outside factors affecting their adoption by both military and consumer markets is given. A survey of intellectual property related to the field is performed, along with a summary of companies active in the area. A rough cost model for production and brief commercialization outlook is presented.

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1. Micro Solid Oxide Fuel Cell Technology

The fuel cell, an energy conversion technology that was first developed in the 19th century by W.R. Grove, is an electrochemical device that creates electricity from fuel. Basically a galvanic cell, a fuel cell, much like a battery, is comprised of an electrolyte, anode, cathode, and a fuel supply. Fuel is oxidized at the anode and oxygen is reduced at the cathode. Electrons leave the fuel cell at the anode and travel to an external circuit to perform useful work, while the ions travel through the electrolyte to complete the circuit. Ideally, this process creates just water vapor and carbon dioxide as exhaust (purely water vapor if hydrogen is used as the fuel), and is considered far cleaner and more efficient than alternative methods of generating electricity such as coal or natural gas combustion. In addition, it is not subject to Carnot efficiency limitations that dictate the efficiency of combustion type energy conversion based on temperature. For this reason fuel cells are being developed for two primary classes of applications in recent times - automotive power and stationary power.

Fuel cells can be categorized in many ways; one of the most common and popular is categorization by electrolyte type. There are five major types of electrolyte used in fuel cells. The solid oxide fuel cell (SOFC) utilizes an electrolyte fabricated from a solid oxide material, typically a ceramic material such as zirconia. The SOFC is currently being developed for use in power generation on a smaller independent scale as either a supplement to the existing power grid or a source of premium power for critical applications. Two other very common types of fuel cell are the polymer electrolyte membrane (PEMFC) and direct methanol (DMFC) fuel cells, both utilize a polymeric electrolyte such as Nafion. These are the focus of a great majority of the high profile automotive and transportation applications currently being touted in the news. The major difference in the functioning of DMFC or PEMFC as compared to SOFC is the ion being exchanged. In SOFC, the oxygen ion is the species of interest which diffuses through the solid oxide electrolyte from cathode to anode. In this case, the reaction products, water vapor and carbon dioxide, are produced at the anode. In PEMFC and DMFC, the proton or hydrogen cation is the species of interest which diffuses. Though fundamentally similar, the proton in this case travels from the anode to the cathode, and the reaction products are produced at the cathode for the PEMFC, as opposed to the anode for the SOFC. The PEMFC/DMFC and SOFC are the two most common types of fuel cells being considered for micro applications due to their solid state construction. Other
types are the alkaline fuel cell (AFC, a long time source of electricity for space applications),
the molten carbonate fuel cell (MCFC), and the phosphoric acid fuel cell (PAFC), which all
employ liquid electrolytes.

The "micro" aspect of the micro solid oxide fuel cell is a more recent concept that
combines MEMS fabrication techniques with the fuel cell concept. Miniaturization brings
some obvious advantages. Integration of a power source with electronics is a major benefit.
Portability is another in that a small power source can be easily carried onboard – one can
immediately see applications in the personal electronics sector. Mechanical robustness can
potentially increase due to solid-state fabrication and design, bringing with it longer lifetimes.
The high manufacturing capacity of silicon-based devices can reduce the overall cost of the
fuel cell and bring the cost per watt to a reasonable level. By micro-fabricating the fuel cell
and controlling the microstructure in the components of the fuel cell, much higher mass
transport and reaction rates can be realized, which can lead to higher efficiencies for energy
conversion. This is a potential advantage due to the fact that the structures of critical
components such as fuel cell electrodes and catalysts can be actively controlled during
fabrication to create extended triple phase boundaries or columnar grains. Other fabrication
techniques such as wafer bonding offer a more reliable way to assemble and seal fuel cell
structures compared to macro assembly techniques. Thin film electrolytes can improve
performance with respect to macro fuel cells ultimately due to decreases in required operating
temperature, potentially leading to longer operating lifetimes.

Both solid oxide and polymer electrolyte fuel cells are being miniaturized today,
typically for use in portable power applications. Critical parameters of these devices are
generally compared to those of the incumbent technology, rechargeable batteries. Currently,
the most important figure-of-merit being used to compare performance is either energy
density (expressed as Watt-hrs/liter) or specific energy (Watt-hrs/kg). where Li-ion batteries
typically achieve 350 W-hr/L. The energy density of certain fuels exceeds this level by an
order of magnitude, potentially (methanol = 4900 W-hr/L and liquid hydrogen = 2500 W-
hr/L), but the quoted values will drop when efficiency and volume of the fuel cell
components are factored in. Micro-fabrication of the fuel cell and supporting systems,
however, will mitigate this dilution of energy density. By shrinking the fuel cell, the fuel
reservoir will occupy a greater percentage of the total volume, and the energy density will be
closer to the theoretical value of the fuel, potentially maintaining the order of magnitude performance increase.

Micro polymeric fuel cells have certain advantages and disadvantages versus micro solid oxide fuel cells. The major advantage is operating temperature. Since the polymeric membrane has adequate proton conductivity at room temperature, it does not need high temperature for operation. The polymeric electrolyte is also easier to process than a solid oxide electrolyte. However, the polymeric fuel cell must run on either hydrogen or methanol fuels. With methanol as the fuel, water must be added to dilute the fuel, and methanol crossover (fuel diffusion through the electrolyte, which decreases efficiency) is a major problem. The membrane must remain hydrated at all times to ensure proton conductivity and it cannot be allowed to dry out or freeze, which constrains operating temperature between 0°C and 100°C, and places some limits on relative humidity within the fuel cell, though recycling of exhaust can help humidify the membrane.

1.1 Operating Principles

The fundamentals of a micro solid oxide fuel cell do not differ from that of macrosize SOFC’s, and differ from other types of fuel cells only by the ion exchange species. The micro-scaling influences parameters such as efficiency, heat transfer, and reaction rates, but the operating principles proceed in much the same way regardless of size. Many of the micro-scaling effects have not been adequately modeled or analyzed. A typical fuel cell is comprised of a stack of many single cells, which operate together to boost voltage output.

The operating principle of a fuel cell is almost identical to that of a battery with one important difference: a fuel cell is continually supplied with reactants while a battery stores its reactants, shutting down when the reactant supply is depleted. As long as the fuel cell receives reactants, it will continue to produce electricity. This is advantageous from the perspective of supplying continuous power; batteries are unable to provide this function, for once their reactant supply is gone, they will require replacement or recharging.

In SOFC’s, this process is carried out at high temperatures (between 600°C and 1000°C) in order to achieve the ionic conductivity required to keep ohmic resistance and ohmic losses to an acceptable level. Heat can be provided by the chemical reactions or, during start up, by an external heat source such as an electric heater. Electricity is produced through a series of electrochemical reactions that release electrons. These reactions include
the reduction of oxygen and the oxidation of a fuel (typically hydrogen). The main components of a single fuel cell and basic operation are shown in figure 1.1-1.

![Figure 1.1-1: Standard solid oxide fuel cell diagram (single cell)](image)

The fuel enters the cell in gaseous form at the anode where it is oxidized with the help of a catalyst. The fuel is oxidized according to the appropriate half-reaction:

- \( \text{H}_2(\text{g}) + \text{O}^\text{=} \rightarrow \text{H}_2\text{O}(\text{g}) + 2\text{e}^- \) (hydrogen)
- \( \text{CH}_4(\text{g}) + 4\text{O}^\text{=} \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{CO}_2 + 8\text{e}^- \) (methane)
- \( \text{C}_4\text{H}_{10}(\text{g}) + 13\text{O}^\text{=} \rightarrow 5\text{H}_2\text{O}(\text{g}) + 4\text{CO}_2 + 26\text{e}^- \) (butane)

Oxygen is provided at the electrolyte/anode interface. The electrons travel from the anode, perform useful work on a load, and end up at the cathode. The oxygen originally enters the fuel cell at the cathode, typically as air. The oxygen is then reduced with the help of a catalyst according the following half-reaction:

- \( \text{O}_2(\text{g}) + 4\text{e}^- = 2\text{O}^\text{=} \)
The oxygen ions travel through the solid oxide electrolyte from cathode to anode by diffusion along the concentration gradient to complete the electrical circuit. The ideal or reversible voltage produced by a single cell can be calculated by comparing the partial pressures of oxygen at the cathode and anode according to the Nernst equation:

$$E_{rev} = \frac{RT}{4F} \ln \frac{P_{O_2(e)}}{P_{O_2(a)}}$$

where $E_{rev}$ is the reversible voltage, $T$ is the temperature, $R$ is the gas constant, $F$ is the Faraday number, and $P_{O_2(e)}$ and $P_{O_2(a)}$ are the partial pressures of oxygen at the cathode and anode, respectively. While the ideal voltage is influenced solely by oxygen partial pressures, non-idealities will introduce other forms of loss in the efficiency of the fuel cell – losses due to ohmic resistance, reaction rate, diffusion of reactants, and activation energy losses. In addition, since the ideal voltage is influenced by partial pressures of oxygen at the cathode and anode, the type of fuel used will impact the absolute value of the voltage. Due to the equilibrium constant of the chemical reactions involved, the oxygen partial pressure at the anode will have a specific value. Using hydrogen fuel as an example, an ideal voltage of 0.997V at 1000K can be calculated. Though one volt is not large enough for most applications, achieving higher voltages is as simple as connecting multiple cells in series, as is done with batteries. A typical fuel cell is comprised of single cells arranged in a stack to increase the overall voltage output to the desired level.

Loss in a fuel cell can come from many different sources and dictates the overall efficiency of the fuel cell. In a single cell, the overall efficiency can be expressed as the product of four sub-efficiencies, thermal efficiency, voltage efficiency, current efficiency, and heating value efficiency.

$$\eta_{FC} = \eta_T \eta_V \eta_J \eta_H$$

In converting chemical energy to electrical energy, if the Gibbs free energy of the reaction is completely converted to electrical energy, then there is a maximum thermodynamic efficiency. The thermal efficiency $\eta_T$ can be expressed as:

$$\eta_T = \frac{\Delta G}{\Delta H} = 1 - \frac{T \Delta S}{\Delta H}$$
The voltage efficiency is based on the actual voltage of the cell as opposed to the reversible voltage that is calculated by the Nernst equation. The voltage efficiency can then be expressed as:

$$\varepsilon_v = \frac{E}{E_r}$$

where $E$ is the actual voltage and $E_r$ is the reversible or Nernst voltage. The loss in voltage is due to four different types of polarization effects and is termed the polarization, overpotential, or overvoltage. These effects are due to activation polarization, diffusion polarization, reaction polarization, and ohmic polarization. Activation polarization is related to the chemical reaction rate-determining steps and the activation energy required to overcome the barrier in the rate-determining step. This rate-determining step can be any one of a number of the steps that need to occur in order for the reaction to proceed, such as adsorption of reactant, electron transfer, or desorption of product [1]. Diffusion polarization occurs when either the reactant stream is depleted or the product removal is too slow to keep up with the reaction rate. This type of polarization is generally dependent on the mass transport properties within the fuel cell. Reaction polarization is similar to diffusion polarization. Ohmic polarization occurs since there is an ohmic resistance to conduction of ions through the electrolyte, electrons through the electrode and interconnect assembly, and contact resistance between cell components.

The current efficiency relates not only to the actual number of electrons transferred to a useful load versus the total electrons available from the chemical reaction, but also to the degree of fuel conversion within the fuel cell. For every mole of fuel consumed per unit time ($df/dt$), the amount of current density produced ($j$) can be calculated as

$$j = zF \frac{df}{dt}$$

where $z$ is the number of moles of electrons produced per mole of fuel (e.g. 2 for hydrogen) and $F$ is the Faraday number. Typically, 100% fuel usage leads to increased diffusion polarization, so fuel cells are operated at less than 100% to offset the loss. Current efficiency can then be expressed as:

$$\varepsilon_j = \frac{j}{j_F}$$

where $j$ is actual current density and $j_F$ is maximum current density (100% fuel conversion).
Finally, heating value efficiency is the ratio of the amount of heat energy of fuel species available in the fuel cell to generate electricity, $\Delta H^*$, to the amount of heat energy included in all combustible species in the fuel gases fed to the fuel cell, $\Delta H_{\text{com}}$ [1].

$$\varepsilon_{HV} = \frac{\Delta H^*}{\Delta H_{\text{com}}}$$

Actual performance of the fuel cell is dependent on each of these efficiencies and the related loss mechanisms. A typical voltage vs. current plot is shown in figure 1.1-2 for illustration.

![Graph](image)

**Figure 1.1-2**: Schematic of the fuel cell voltage versus current density and power density vs. current density.

Regions of loss are identified in this plot for low, medium, and high current densities. At the low current density, losses are primarily due to activation polarization – processes such as adsorption, desorption, electron and ion transfer, etc., and is responsible for the steep initial drop in voltage. At medium current density, the majority of losses come from the ohmic or resistance polarization. This region is linear due to the overall internal resistance of the cell and its components (cathode, anode, and electrolyte). Finally, at high current density, mass transport becomes the limiting factor and voltage begins to drop more strongly since the flow of reactants is not enough to keep up with the high current draw. This implies that there is a maximum or optimum power output for a fuel cell based on the current density, which is also shown in figure 1.1-2 on the secondary axis. In practical use, it is likely that fuel cell stacks
will be optimized to run at the power peak, and thus the stack will have an ideal voltage greater than that required – for example, use of a 10V stack to power a 7V load. In addition, as current demand increases, the easiest way to meet increased demand is simply to increase the area of the fuel cell, at the expense of overall size. However, increasing current density can be achieved by fine-tuning the design of the fuel cell components. Power density of just over 1 W/cm² has been reported [2].

Micro-scaling the assembly has a few interesting effects on the performance of the fuel cell. Mass is significantly decreased. The surface area to volume ratio greatly increases, and thus heat and mass transfer effects are drastically increased. This can be beneficial during start up since the amount of heat input required to initially heat up the system is much lower and the heat transfer rate is much higher, leading to extremely rapid heat up time. Conversely, the heat transfer rates increase to such a degree that thermally insulating the fuel cell itself in a micro-scale scenario becomes very challenging. An increase in overall mass transfer rate can help to reduce the amount of diffusion polarization and increase efficiency. Other advantages pertaining to the end use of a micro fuel cell will be addressed in the applications section – these are typically different depending on the situation.

Each component of a micro fuel cell has certain requirements that must be met. There are two common requirements among all the components. The first requirement is phase stability – the components or materials used must all be chemically and morphologically stable with respect to their adjacent components over long periods of time. The second is thermal compatibility – the materials must have similar thermal expansion coefficients to minimize thermal stresses that will occur during the thermal cycling of the device. Past this, requirements for components vary; some require high density and no interconnected porosity, while others require high levels of interconnected porosity. Some require ionic conductivity while others require electronic conductivity, and some require both.

1.1.1 The Electrolyte

The electrolyte functions as the conductor between the electrodes and also as a gas diffusion barrier. The electrolyte has key requirements. It needs to possess conductivity with respect to the ion being conducted, in this case oxygen, so ionic conductivity must be high. Electronic conduction, however, needs to be very low to prevent loss of electrons via short-
circuiting across the electrolyte. Mechanical stability and low porosity is required to prevent gas diffusion from one side to the other, and in some cases provide mechanical strength to the fuel cell stack. Chemical or phase stability is required to prevent reaction with adjacent materials that may adversely affect material properties and ultimately the performance of the fuel cell. Finally, the electrolyte must have a similar thermal expansion to the adjacent structures to minimize the thermal stresses induced upon heating and cooling cycles. Such a stringent set of requirements quickly narrows the materials systems that can be combined for use in a solid oxide fuel cell.

Typical materials for solid oxide electrolytes are those with cubic fluorite crystal structure (MO$_2$), such as stabilized zirconia (ZrO$_2$) or ceria (CeO$_2$). The fluorite structure can be doped with divalent or trivalent cations to produce oxygen vacancies and thus increase the oxygen ion diffusivity dramatically. Dopants for the electrolyte material typically used include yttria (Y$_2$O$_3$), La$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, CaO, and SrO. Dopants work basically by altering the electroneutrality of the system — in essence, for every two trivalent cations introduced as a substitute for a the tetravalent cation (for example Y$^{3+}$), one oxygen vacancy (V$_{O}^{−}$) must be created to maintain charge neutrality. Introduction of vacancies into the structure however is typically not enough and high temperatures must be achieved to boost conductivity further. Conductivity follows Arrhenius behavior — being an activated process, it is exponentially dependent on temperature. Generally, conductivity can be described as

$$\sigma = A_e \exp \left( \frac{-E_e}{kT} \right)$$

where $\sigma$ is the conductivity, $A_e$ is a pre-exponential constant, $k$ is the Boltzmann constant, and $E_e$ is the activation energy for conduction (assuming constant activation energy over the temperature range under consideration). Since the resistance of the electrolyte will impact the performance of the fuel cell negatively, steps must be taken to reduce the resistance. Accordingly, one way to achieve this is to increase conductivity. Thus, to achieve the appropriate conductivity, the solid oxide fuel cell must be run at relatively high temperatures, typically above 1000°C for most large systems. There are other ways to achieve a low electrolyte resistance; micro fuel cells seek to do this by decreasing the thickness of the electrolyte by many orders of magnitude.

Ionic conductivity can also be affected by changes in oxygen vacancy density, which is dependent on oxygen partial pressure. Since the electrolyte is exposed to both the anode
(reducing) and cathode (oxidizing) conditions, it must be stable in both types of atmosphere. The ultimate range of oxygen partial pressures that the electrolyte can operate in before becoming strongly electron conducting can be calculated. Typical oxygen partial pressures in most fuel cells are limited to atmospheric pressure or slightly above for simplicity of design. From this, defect domains can be estimated in the standard manner and the range of partial pressures in which the fuel cell electrolyte will function properly (it will mostly conduct ionically and not electronically).

1.1.2 The Electrodes – Anode and Cathode

The electrodes perform two primary functions: the first is to provide reaction area for the adsorption of gaseous reactants. The second is to allow electrons to travel towards the load in a timely manner. The electrode is sometimes called upon to provide mechanical support for the entire stack; this function can be accommodated by the electrolyte or interconnect as well. Much of the fuel cell function occurs at the electrodes, and thus optimizing material properties has a strong influence on the overall performance of the fuel cell.

A key parameter for the electrodes is the area of triple phase boundaries. These triple phase boundaries are particularly important since the electrochemical reaction requires both electronic and ionic diffusion to occur. Since the electrolyte provides the ionic diffusion path and the electrode provides the electronic diffusion path, these two materials must be in proximity for the reaction to proceed. In addition, the gaseous reactants of course must be supplied – they must be allowed to reach the boundary between electrode and electrolyte, thus introducing the third phase – porosity. Unlike the electrolyte, the electrodes must maintain a high degree of porosity to allow gas diffusion of reactants. A typical triple phase boundary representative of the anode is shown in figure 1.1.2-1. In this figure, the electronic conductor is shown in black, the ionic conductor in gray, and the porosity or gas phase is shown as empty space or in white. White arrows show the motion of ions from the electrolyte to the triple phase boundary, while gray arrow shows the movement of electrons. The black arrow shows the gas flow of the reactant, in this case, fuel.
Figure 1.1.2-1: Electrode triple phase boundary (shown where arrows converge) [3]

Other requirements for electrode materials are the same as the electrolyte—chemical stability, phase stability, and thermal expansion match to adjacent components.

The anode provides sites for adsorption and electrochemical reaction of the fuel (hydrogen) and also can be used to catalyze the incoming fuel stream into hydrogen if necessary. The overall effectiveness of the anode depends mainly on its catalytic activity. Being immersed in a fuel gas atmosphere, it must be stable under reducing conditions. Typical anodes for solid oxide fuel cells are cerments (ceramic-metal composites) that contain metals such as nickel, cobalt, or other noble metals, and a ceramic matrix such as zirconia. The electrochemical oxidation occurs solely on the metallic portion of the cermet anode, with the ceramic matrix serving as a thermal expansion matching component and also as a sintering inhibitor. At the high operating temperatures of the fuel cell, the porous anode will tend to sinter into a solid dense structure if it is fabricated solely from metal, and defeat the flow of reactants necessary for the fuel cell to function. Materials selection is important in the design of the anode, but nickel is typically used as the metal due to its low cost and availability (as opposed to use of platinum or silver). Zirconia is typically used as the ceramic matrix due to the fact that it is also commonly used as the electrolyte and is thus a perfect match (thermal expansion and chemical stability).

The cathode functions as a catalyst for adsorption of oxygen and operates in a predominantly oxidizing atmosphere. Materials for use as a cathode in macro fuel cell
technology include doped perovskite structures (ABO$_3$) such as strontium doped lanthanum manganite or lanthanum cobaltite, both of which have a reasonably good thermal expansion match to zirconia. Again, materials selection is strongly dependent on thermal expansion match since the fuel cell will potentially undergo thousands of thermal cycles over its lifetime.

It is desired to have an electrode with mixed ionic-electronic conductivity (MIEC). Mixed ionic-electronic conductivity in the electrode can benefit the efficiency of the fuel cell by allowing not only electrons but also oxygen ions to diffuse through the electrode structure – thus expanding the effective ‘triple phase boundary’ available for reaction. Maximization of this ‘triple phase boundary’ is known to have great impact on the overall efficiency of the fuel cell.

1.1.3 The Interconnect and Stack Design

Since fuel cells are typically composed of multiple single cell units connected in series, a way to assemble them into a stack is necessary. Another component not yet discussed now becomes involved, namely, the interconnect. The interconnect has all the requirements of the electrolyte in that it must be stable in oxidizing and reducing atmospheres, be fully dense to preclude any gas diffusion, have chemical and phase stability with respect to the adjacent components (electrodes), and also have as near a thermal expansion as possible to the adjacent components. The primary difference is that the interconnect, unlike the electrolyte, needs a very high electronic conductivity instead of ionic conductivity. Interconnect materials range from metals (Ni-based alloys) to conductive ceramics such as lanthanum chromite.

There are a number of different designs for fuel cells, but they generally fall into two categories, planar and tubular. Typical planar type fuel cell stacks can be seen in figures 1.1.3-1 and 1.1.3-2. This is the classical design for a fuel cell stack, where the repeat unit is electrode, electrolyte, electrode. The repeat units are physically stacked next to each other to create a series connection and achieve higher output voltage. This design is advantageous in that it is simple and effective. The monopolar design, shown in figure 1.1.3-1, uses fuel cells that share gas chambers but are electrically insulated from one another. The interconnects are long conductive paths similar to wiring. Interconnect resistance becomes more appreciable in
this design because of the path length, but rerouting the path in case of cell failure is relatively easy [8].

![Monopolar Stack Design](image1)

**Figure 1.1.3-1: Monopolar stack design (C: Cathode, A: Anode, E: Electrolyte)**

The bipolar design, shown in 1.1.3-2, uses interconnect plates instead of wires to provide a series connection for the fuel cell stack. These plates face both fuel and air environments and connect cathode to anode directly. Separate channels within the interconnect provide spaces for the fuel or air to flow through. This decreases the interconnect resistance, but failure of one cell in the stack automatically causes failure of the entire stack [8].

![Bipolar Stack Design](image2)

**Figure 1.1.3-2: Bipolar stack design (C: Cathode, A: Anode, E: Electrolyte)**

The simplicity of the planar design is offset somewhat by the complexity in fuel and air delivery, however. Since anodes and cathodes are staggered, fuel and air inputs must also be staggered. The second type of fuel cell stack design seeks to alleviate this problem. The
tubular design, pioneered by Siemens-Westinghouse, allows fuel and air to flow in simpler manner (see 1.1.3-3). This design allows the fuel to flow over the exterior of a tube, while the air flows over the interior of the tube. Variants of this design are based on the physical support structure of the tube, which can be anode supported, cathode supported, or electrolyte supported. Stacks are created by aligning tubes in an array and interconnecting the tubes' outside surfaces.

Figure 1.1.3-3: Tubular SOFC design (Source: Siemens Westinghouse)

Some designs allow air to enter the stack from one side and exit the opposite side, with the fuel flowing in from the adjacent side and exiting the opposite side (see 1.1.3-4). This is a simple variant of the bipolar planar design and helps to consolidate fuel and air flows for the stack.
In another variation, so-called banded or flip-flop designs allow formation of the electrolyte, anode, and cathode on one plane (see 1.1.3-5) to some extent. The banded structure allows fuel and oxidant to be separated into two reaction chambers, but the tradeoff is the crossover of one of the electrodes from cell to cell, which complicates fabrication. The flip-flop design allows a completely planar fabrication process with a minimum of levels, but multiple sealed reaction chambers are required for fuel and oxidant.

For micro-fabrication, planar designs seem to be the most practical so far due to their compatibility with thin films processing techniques. It is likely that a tubular thin film design is being pursued elsewhere since this design is fairly robust, simple, and because there are many years of operating data available (in the kilowatt scale design).
1.1.4 Fuel types

The device must produce electricity from another source, and the source of the electrons in this case is the fuel. The standard fuel used is hydrogen. Polymer electrolyte membrane fuel cells run almost exclusively on this fuel, the major exception being methanol. Note that while hydrogen has an extremely high specific energy (watt-hours per unit mass), its energy density (watt-hours per unit volume) is very low due to the density of hydrogen. It is unlikely that micro fuel cells will run on solely hydrogen due to storage issues, and methanol is the fuel of choice for polymeric fuel cells. However, solid oxide fuel cells, due to their high operating temperature, have the capability to run on many different types of hydrocarbon fuels. It has been pointed out that in polymer fuel cells, due to the catalysts used, carbon monoxide must be completely extracted from the fuel as it significantly reduces the catalytic activity by binding to active sites. In solid oxide fuel cells, conversely, carbon monoxide can actually be oxidized and used as fuel. Some fuels and their approximate energy densities are given in Table 1.1.4-1. The future target value for a lithium ion battery today [7] is included for comparison.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Energy Density (Watt-hrs/liter)</th>
<th>Specific energy (Watt-hrs/kg)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid hydrogen</td>
<td>2,600</td>
<td>39,000</td>
<td>-0.06</td>
</tr>
<tr>
<td>Methanol</td>
<td>4,900</td>
<td>6,200</td>
<td>0.79</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6,100</td>
<td>7,850</td>
<td>0.78</td>
</tr>
<tr>
<td>LNG</td>
<td>7,216</td>
<td>12,100</td>
<td>0.60</td>
</tr>
<tr>
<td>Propane (liquid)</td>
<td>7,000</td>
<td>13,900</td>
<td>0.51</td>
</tr>
<tr>
<td>Butane</td>
<td>7,700</td>
<td>13,510</td>
<td>0.57</td>
</tr>
<tr>
<td>Gasoline</td>
<td>9,000</td>
<td>13,500</td>
<td>0.67</td>
</tr>
<tr>
<td>Future Li-ion [7]</td>
<td>550</td>
<td>440</td>
<td>-1.25</td>
</tr>
<tr>
<td>Li-ion reaction</td>
<td>1,350</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

It should be noted that these energy densities are the theoretical values; they represent the ideal or maximum energy density that could ever possibly be achieved. Li-ion batteries suffer from inefficiencies in packaging which reduces their energy density. For reference, the Li-ion reaction energy density (theoretical) is also shown in Table 1.1.4-1 for comparison. It is however many times lower than the values for the hydrocarbon fuels shown.
Use of the fuel in a solid oxide fuel cell can be either through direct oxidation or through reforming. Reforming reactions convert hydrocarbon fuels into hydrogen and carbon dioxide, utilizing water as a reactant (typically from rerouted exhaust streams). The basic reactions for catalytic reforming of a hydrocarbon fuel are [8], [9]:

\[ C_nH_m + nH_2O \leftrightarrow nCO + \left( n + \frac{m}{2} \right)H_2 \]
\[ C_nH_m + nCO_2 \leftrightarrow (2n)CO + \left( \frac{m}{2} \right)H_2 \]

The reactions are endothermic and require heat input, which can be supplied by an external source initially (electric heater) and then possibly by either partial oxidation of the fuel or utilization of waste heat produced by the fuel cell. Both the hydrogen and the carbon monoxide produced can then be oxidized by the fuel cell to produce electricity. Due to the low activation polarization of hydrogen oxidation, reforming allows higher voltages. Direct oxidation of fuel is possible using appropriate anode materials such as copper doped ceria cermets [10] and makes the system integration easier in that reforming is no longer necessary. However, direct oxidation increases activation polarization and thus decreases the overall efficiency of the fuel cell. It is not obvious which of either direct oxidation or reforming of hydrocarbon fuel will be more efficient.

1.1.5 Fuel delivery systems

Fuel delivery is the last component and is the key differentiator between batteries and fuel cells. Whereas batteries (primary) convert chemical energy to electrical energy in the same manner as fuel cells, their reactant storage is limited and non-replenishable. Secondary batteries can be recharged but require electrical input to its reactants from an outside source. Further, the reactants tend to be dense and have low energy density. Fuel cells have the advantage of being able to use higher energy density fuels such as hydrocarbons, the potential convenience of refueling instead of recharging, and a more consistent power output with lifetime as compared to batteries.

Obviously, fuel and air will need to be stored onboard and delivered somehow to the electrodes. Typically, capillary, gravitational, or pressurized systems have been utilized to deliver the fuel and air to the fuel cell in large stationary systems. However, in micro-scale
systems, the issue with fuel delivery becomes more complicated. While gravitational fuel delivery is satisfactory for large stationary fuel cells, the size of a micro fuel cell almost demands its use in decidedly non-stationary applications, and orientation of the fuel cell will not be constant. In other words, the fuel delivery system will have to work both upside-down and right side-up, and under turbulent conditions.

Among pressurized systems, a MEMS style pump or pressurized fuel cartridge or ampoule has been imagined. In this case, the fuel pump needs to be designed, will contain moving parts, requires power, and will add complexity to the system. The simpler pressurized cartridge runs the risk of delivering varying pressure to the fuel cell as the fuel it contains is used up – thus impacting performance. Elastic or mechanical pressure on a fuel container perhaps in the form of a clamp may alleviate this problem. Capillary action is a more passive method for fuel delivery, and can be achieved by creating microchannels in the interconnects that lead to the fuel reservoir.

Air pressure will almost certainly need to be supplied to the fuel cell given that the diffusion of oxygen through the electrolyte will be driven by the concentration gradient between the cathode and the anode. A micro air pump or some other means of continually supplying air to the cathode will be required. Higher oxygen concentration gradients will increase the driving force for diffusion between cathode and anode.

Fuel delivery is an important part of the integration of a micro-fabricated fuel cell stack into a portable electricity source. The design of the stack and the necessary components plays a critical part in the technological success of the micro solid oxide fuel cell concept.
1.2 Micro-Fabrication and Design

Fabrication of a solid oxide fuel cell using standard micro-fabrication techniques is difficult. In fact, there is no manufacturing technology that allows for production of micro solid oxide fuel cells in existence today. While processes do exist for production of certain components of micro solid oxide fuel cells, and there are many analogous manufacturing methods that could be applied, there remain challenges in fabrication and, more importantly, integration.

Traditional microelectronics processing can be used to fabricate the thin films that make up the core components of a micro solid oxide fuel cell. The electrolyte, the anode, the cathode, and the interconnects will all be formed using thin films deposition techniques such as physical vapor deposition or chemical vapor deposition. Patterning is accomplished by use of standard photolithography techniques.

The fabrication method for a single cell can be repeated to create a stack. The substrate for initial deposition and support of the stack is typically silicon. A low stress silicon nitride is deposited on the silicon substrate to electrically insulate the stack and to serve as an etch stop to create a window on the backside of the substrate via photolithography and anisotropic wet etch [11]. The anode, electrolyte, and cathode are deposited sequentially on the silicon nitride layer and patterned to create the appropriate stack design. Interconnects can be deposited either anode-to-cathode for series connections (voltage increasing) or anode-to-anode for parallel connections (current increasing). Anode-to-cathode connections on the same substrate will require a banded or flip-flop design as shown previously in figures 1.1.3-3 and 1.1.3-4. Anode-to-anode connections are simpler in that they are in the same plane, and stack formation could then be accomplished by appropriate connection of separate substrates. A thin film electric heater can be deposited on the electrolyte for maintaining temperature and keeping ionic conductivity at a satisfactory value. A sample schematic showing a cross section of a microfabricated single cell is shown in figure 1.2-1.
Figure 1.2-1: Microfabricated single cell [12]

This single cell unit can be repeated multiple times on the same substrate to create a 'stack' or array of cells to achieve the desired voltage and current characteristics. Fuel and air channel patterns are etched into separate substrates and bonded to the original substrate’s top and bottom surfaces to create a two chamber design and facilitate air and fuel flow through the array of cells. Inlets for air and fuel can be created either through the substrate or via side ports depending on the desired design. As can be imagined, there is much flexibility in designing the required fuel and air system, interconnect pathways, and the anode/cathode/electrolyte core unit to achieve different goals. With this review of a basic fabrication scheme, different challenges now arise.

Thermal expansion matching of components to the deposition substrate is a major challenge, though the thin film nature of the components may tend to reduce the overall thermal stresses incurred by thermal expansion mismatch. In typical operation, the fuel cell stack (electrodes, electrolyte, substrate, and interconnect) undergoes thermal cycling as power is demanded in the application. This leads to stresses in films which result from slight mismatches in thermal expansion coefficient from one film to the next. Materials selection is critical in matching the thermal expansion as closely as possible to minimize the thermal stresses that can occur during thermal cycling. Yttria stabilized zirconia for example has a coefficient of thermal expansion (CTE) of about 10 ppm/C. Silicon has a CTE of about 3 ppm/C. Assuming a CTE-matched stack, the stresses will arise in the electrode/substrate
interface. Depending on the zero stress temperature (most likely the deposition temperature), stresses in the thin film components will be either compressive or tensile. For example, if the deposition temperature is 200°C and the operating temperature is 500°C, the thin film components will be in a compressive state during operation, as the thin film zirconia stack will expand more than the substrate will allow. Conversely, as the stack cools to room temperature, the thin film stress state will go from compressive, to zero stress, and finally become tensile.

Chemical stability of components within the stack is also important. The typical material used as the solid oxide electrolyte, yttria-stabilized zirconia (YSZ), is used in concert with strontium doped lanthanum manganite (LSM) as a cathode material, and a nickel-YSZ ceramic-metal (cermet) composite as the anode material. Stability of this material system is excellent, provided that the system remains below the temperature at which lanthanum zirconate phases can form at the cathode-electrolyte interface. This compound tends to block ionic conduction from the electrolyte to the cathode. New cathode materials are being sought to prevent this problem, and provide higher conductivity. Two promising new cathode materials are La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (LSCF) and Sm$_{0.8}$Sr$_{0.2}$CoO$_3$ (SSC) [11]. Anode materials that provide better performance than the current Ni-YSZ cermet include Cu-CeO$_2$ cermets. These provide high catalytic activity and also appear to circumvent coking problems that plague the traditional Ni-YSZ systems [10,13].

Stability of these films over time is critical to the successful operation of the fuel cell. Thin films deposition is done at a fairly low temperature, and subsequent operation at a higher temperature will quickly reveal any metastable structures or phases in the thin films. Recent work at MIT on a thin film YSZ electrolyte has shown metastable grain structure which eventually leads to high tensile stress and fracture [11]. At temperatures sufficient to enable solid state diffusion, the high surface energy associated with extremely fine grains (10-20 nm as deposited) can lead to rapid coarsening and shrinkage. This is especially problematic in the electrodes, where structures must remain porous to allow gas diffusion. Deposition also tends to create some degree of non-crystallinity in the film, which results in a lower density. Over time, the film may recrystallize, shrinking the film and causing tensile stress. A higher deposition temperature may help to prevent some of the metastability introduced into the films, and lower operating temperature will help extend the useful life of the films. While lowering the operating temperature will reduce the issues associated with in-situ sintering of the fuel cell
components, removing the meta-stability associated with the microstructures created remains a difficulty.

Thermal management of components is another major challenge. Since the stack itself is very small, and planar in nature, the surface area to volume ratio is very high. Thermal transfer is thus very high, and maintaining an operating temperature of just 400°C - 600°C will require either very effective thermal insulation or input of heat from an external source to achieve a steady state. Additional external heat can come from oxidation or combustion of unused fuel gas in the exhaust stream, or from an electrical resistance heater. In fact, thermal management is the major obstacle to technical success for micro solid oxide fuel cells. Heat loss can occur via conduction, convection, or radiation. In addition, the exhaust gas streams will carry away heat. Minimizing the heat loss can entail building the stack in a vacuum sealed package to reduce convection. Conductive heat loss can be minimized by physically removing conduction paths and suspending the stack with the minimum number of thermally insulating support structures. Finally, radiative heat loss can be minimized by creating a reflective cavity for the stack to reside in. These challenges have been addressed in part by work on a high temperature suspended micro-reactor at MIT [14].

There are also many sources of heat inherent in the fuel cell; inefficiencies in the fuel cell are a convenient way to gauge heat generation. A 10W fuel cell at 30% efficiency (assuming 100% fuel efficiency) will produces 3W of electricity and 7W of heat. As fuel efficiency decreases, the heat produced will decrease since the fuel will either be swept away in the exhaust gas along with any energy that remains with it, or recollected. Thus heat dissipation in the fuel cell is also an issue. For comparison, typical notebook computer processors have a thermal design power of 30W, while desktops can be as high as 70W. Thermal design power is the maximum amount of power the device is required to dissipate. Using thermal management technologies like heat pipes, heat sinks, and cooling fans, the processor is kept below about 100°C. It may be possible to utilize waste heat in the fuel cell to feed reforming reactions, which are generally endothermic. Heat could also be dissipated in the exhaust stream. In general, heat loss becomes the greater challenge as the stack size and power output become smaller, and cooling the greater challenge as the stack size and power output become larger.

There are some advantages of micro-fabricated fuel cells over their traditionally fabricated counterparts, however. Each component in the fuel cell will benefit from the micro-
scale to some extent. One major advantage in going to a micro-scaled system is the reduced diffusion length for oxygen ions to travel, as the electrolyte thickness is potentially on the nanometer scale, as opposed to macro scaled systems with millimeter scale thickness. This will reduce the resistance of the electrolyte and reduce the ohmic losses that contribute to the overpotential of a fuel cell. An example of the effect on thickness on the voltage output of a hypothetical fuel cell is shown in figure 1.2-2.

![Graph showing the effect of electrolyte thickness on voltage output.](image)

**Figure 1.2-2 : Effect of electrolyte thickness on voltage output for a hypothetical fuel cell with an electrolyte of 100um thickness vs. one with an electrolyte of 50um thickness.**

In a related advantage, the high temperatures required to bring macro scaled electrolytes' resistance down to acceptable levels may be precluded with a thin-film electrolyte. This has advantages in increasing the operating lifetime and reducing thermal expansion stresses by decreasing maximum operating temperature. Combined with proper materials selection, a micro-fabricated fuel cell has the potential to run hundreds of degrees cooler than its macro-scaled counterpart. In determining materials for use as the electrolyte, it can be useful to set an area-specific resistance (ohms-cm$^2$) to evaluate the compromise between operating temperature, material conductivity, and electrolyte thickness [15]. As can be seen in figure 1.2-3, materials with either inherently higher conductivity or lower thicknesses will allow operation at lower temperatures.
Figure 1.2-3: Specific conductivity versus temperature for some typical SOFC electrolyte materials. [15]

If the area specific resistivity (L/σ) is set at 0.15 ohm-cm², and electrolyte thickness at 15μm, a boundary or cutoff as represented by the arrow on figure 1.2-3 can help determine the required operating temperature of different materials. For example, a 15 μm thick electrolyte made from (ZrO₂)₀.₉(Y₂O₃)₀.₁ requires an operating temperature of about 700°C, as shown by the intersection of the arrow and its characteristic conductivity plot. However, Ce₀.₉Gd₀.₁O₁.₉₅ at the same parameters would only require an operating temperature of 500°C. Using thin films deposition, electrolyte thickness can be made as low as 150 nm. Using this parameter, the required operating temperature for (ZrO₂)₀.₉(Y₂O₃)₀.₁ drops significantly, to 400°C. Ce₀.₉Gd₀.₁O₁.₉₅ at this thickness is well below 200°C. CeO₂ exhibits volumetric expansion with oxygen vacancy concentration, however, introducing additional stress to the system.

Micro-fabrication of the electrolyte can be performed by thin film deposition; chemical vapor deposition or physical vapor deposition. These techniques allow the formation of films with controlled properties and composition, and could allow deposition of specific microstructures that would improve the performance of the electrolyte. For instance, columnar microstructures in the electrolyte may increase diffusion of oxygen ions from cathode to anode by introducing high diffusivity paths along grain boundaries. Traditionally formed electrolytes have more equiaxed grain structures which create a more tortuous path and present blocking grain boundaries to diffusing ions. In addition, purposeful creation of structures in the
electrodes that would maximize the triple phase boundary could make the reaction proceed more rapidly.

In micro fuel cells, the short diffusion distance inherent in the thin film structures being fabricated for the fuel cell will reduce the degree of diffusion polarization and thus increase the overall efficiency. Mass transport rates should be higher than in the macro scaled fuel cell systems and may lead to small increases in fuel utilization efficiency.

The greatly reduced mass of a micro-scaled system is beneficial in regards to the start up time of a solid oxide fuel cell. With less mass to heat up initially, combined with a lower standard operating temperature, the micro solid oxide fuel cell will be able to heat up in a fraction of the time it takes for a large SOFC system to heat up. This is mainly due to the decreased thicknesses of all the components involved in the stack – the electrodes, electrolyte, and interconnects.

Finally, the scaling of the system has potential benefits on the overall energy density of the system. A larger fuel cell component (including fuel delivery, electrodes/electrolyte, interconnects) in a constrained volume (we can assume a laptop battery of about 350 cc) will effectively decrease the energy density of the system. A micro scaled fuel cell component, taking up less volume, will allow the fuel reservoir to be larger, and will increase the energy density of the system. Thus miniaturization of the operating components, the 'engine', of the fuel cell system will be beneficial for portable power in that more fuel can be stored on board. The compromise is of course in overall power generation – the requirements for active area do not change much in a micro-scaled system and thus achieving 100W or more in micro-scaled fuel cell will necessarily entail increasing the size of the stack.

Despite the major technical challenges, the potential benefits of a micro-scaled fuel cell lead to benefits in small scale power generation. The application of the technology to existing areas in portable electronics is obvious. Now critical evaluation of micro solid oxide fuel cells as compared to other technologies, and its application to useful purposes is necessary.
2. Technological Potential

The purpose of fuel cells is the generation of electricity, and this clearly limits its application to those areas where electricity is required. However, due to the broad scope of electric power systems, and electricity's application in almost every aspect of human life today, it is a daunting task to analyze every possible application of electric power where micro SOFC's might be employed.

Despite this, two main categories can quickly be discerned. The first is in regard to existing power applications. In defining this category, a quick review of existing applications indicates that those that are stationary or located in areas with easy access to the power grid are probably out of reach for micro fuel cells, unless convenience and cost become competitive with national utilities, which is highly unlikely. The standard cost for power from the grid is on the order of ten cents per kilowatt hour, where the cost of power from a Li-ion battery today ranges from $2000-$9000 per kilowatt hour of capacity. This fact points in the direction of portable, mobile, or remote electronics and appliances, which is a huge existing market with a strongly entrenched incumbent technology: batteries. Primary batteries almost exclusively fulfill the power requirements of low-end electronic appliances due to their low cost. In a recent report [16], projected global battery sales (primary and secondary) for 2004 were approximately $60 billion, with 1999 total sales reported to be around $41 billion. In this area, as a displacement technology, the advantages and disadvantages of micro fuel cells vs. batteries, especially rechargeable batteries, will be outlined and critically reviewed.

The second category exists in an undefined area – one in which the micro fuel cell is the enabler. In this category, the micro fuel cell will enable applications that were previously unfeasible due to factors related to performance, cost, or convenience.

2.1 Existing Applications and Critical Comparison

There are many applications within the mobile electronics sector, and new ones are constantly being developed. A very common and predictable trend in this sector is "better, smaller and lighter" – it is clear that mobility is critical; wires that tether the device (and the user) to a stationary object for data, or more commonly, power – contradict mobility. Power requirements are also continually increasing. Imaging devices such as digital cameras and
camcorders continually shrink while their LCD displays get larger and brighter. Laptops strive to be equivalent to desktops in both computing power and display brightness with the added requirement of very low weight and low profile. So-called ‘convergence’ devices strive to combine multiple functions on-board a single device, 3G mobile phones are just one example of a combination of high drain devices including digital cameras, personal digital assistants, and digital communications. Common among all these applications’ power requirements is that the battery lifetime needs to be very high but at the same time as light and small as possible. Indeed, the smaller these devices become, the larger the battery becomes in proportion to the device. It is well known that shrinking the battery necessarily decreases the energy carrying capacity of the device. Unfortunately, high tech devices are not only much smaller than their predecessors, but their power requirements are also greater than those of the older devices. Thus there is a significant need for more energy in a smaller, lighter package. The one parameter that is critical to the issue is energy density, which is a measure of the amount of energy that can be stored per unit volume or per unit mass. This is the primary comparison between energy alternatives in the portable power sector. Energy density is typically expressed in Whr/L, while another related parameter, specific energy, is expressed in Whr/kg. Current rechargeable battery technology is at best 300 Whr/L, with performance increases expected to top out at 550 Whr/L [7]. As stated before, the highest possible energy density of a fuel cell is that of the fuel; typical values of some common fuels were listed in Table 1.1.4-1. Methanol is quoted very often in the literature, and has an energy density of about 4,900 Whr/L. Butane, a common fuel used for lighters in the consumer sector, has an energy density of about 7,700 Whr/L. However, given the efficiencies of the fuel cell, the ratio of the fuel cell volume to the fuel reservoir volume, and the specific application the fuel cell is being targeted for, the energy densities of the fuel cell will most certainly not be as high as the theoretical value.

For example, the theoretical energy density of the lithium-ion reaction is 1,350 Whr/L. Due to efficiency and packaging constraints (between 30%-40%), the useful or practical energy density drops to around 350 Whr/L [17]. Given this analog, we can use rough assumptions on packaging efficiency and overall efficiency to find the energy density of ‘first generation’ micro solid oxide fuel cells, and compare it against the incumbent technology: batteries.
For a standard fuel cell – efficiency being calculated as a product of the thermodynamic efficiency, voltage efficiency due to polarization losses (activation, diffusion, reaction, ohmic), current efficiency (also known as fuel utilization or fuel efficiency), and heating value efficiency – an overall efficiency of 30% is assumed for this exercise. Actual efficiencies of the micro-SOFC are unclear, but this assumption is in line with the current state of the art, and future progress in the field may boost the efficiency to 50%. Given an overall efficiency of 30%, the conversion of fuel to electricity immediately drops from the potential of 7,700Whr/L to 2,310Whr/L. This value is still much higher than the standard Li-ion rechargeable battery on the market today, and is about twice that of the theoretical value of the lithium ion reaction.

The second factor to take into account is the overall volume of the system, the relative volume of the fuel cell, and the volume of the fuel reservoir to get an idea of the packaging efficiency. An assumption needs to be made about the overall size of the fuel cell stack and supporting components, as these take up volume without adding any additional energy to the system. For example, a packaging efficiency of 30% (the current value for Li-ion batteries) combined with a 30% system efficiency solid oxide fuel cell would result in a total efficiency of 9%, which results in an overall energy density of 693 Whr/L. While this is slightly less than twice the current energy density of Li-ion batteries, thin films fabrication and microelectronics techniques may be able to help in boosting packaging efficiency.

There have been many publications and patents dealing with thin film solid oxide fuel cell electrolytes (TF-SOFC), many of which are fabricated for the express purpose of lowering the operating temperature requirements of the fuel cell, which places constraints on fabrication and materials. The operating temperature needs to be high since the conductivity of the electrolyte material is low; in fact it is so low that there is serious performance loss. Reduction of this loss can be approached in two ways: either by changing the conductivity of the material, or by changing the size and shape of the material. As stated before, solid oxide fuel cells typically run at 600°C-1000°C to achieve a low electrolyte resistance, as material conductivity follows Arrhenius behavior. However, another method used to decrease electrolyte resistance is by altering its shape and size. Electrolyte resistance can be calculated by

\[ R = \frac{L}{\sigma A} \]
where \( R \) is resistance (ohms), \( \sigma \) is the conductivity (ohm-cm\(^{-1}\)), \( L \) is the thickness of the electrolyte (cm), and \( A \) is the area (cm\(^2\)). Thus one way to reduce resistance is by decreasing the thickness (\( L \)) of the electrolyte dramatically. This can be done by depositing the electrolyte as a thin film. Increasing the area and conductivity are two other ways to improve efficiency, though area increases necessarily increase the size of the electrolyte, and increasing the intrinsic conductivity is a more difficult prospect. Electrolytes fabricated from zirconia with thicknesses as low as 100 nanometers have been engineered at MIT [18]. Thin film electrodes and interconnects are also under development in order to achieve a completely microfabricated solid oxide fuel cell stack. With these techniques, a better estimation of the probable packaging efficiency can be made.

2.1.1 Energy Density Comparison

With expectations of component thicknesses to be in the submicron range, we can attempt to calculate the volumetric power density of the device in W/cm\(^3\). For a specific power output (based on the application), we can estimate the volume of the fuel cell stack required. Taking this stack size, we can find the volume available for the fuel cell on the device itself (by comparing against the existing power supply), and then calculate a rough packaging efficiency. Larger size applications such as a notebook computer will enable larger overall volumes for fuel storage, and practical energy density will go up. Higher power requirements, however, will increase the overall size of the fuel cell stack, and practical energy density will go down. The actual energy density depends on the compromise between power demand and volume available; very small yet high power devices will have the lowest energy density values, while larger low power devices will have the higher energy density values. This is assuming of course that the maximum power demanded by the device will be fulfilled solely by the fuel cell. It is well known that some devices, especially digital devices, can demand large spikes of power that fuel cells are unequipped to handle. Integration of a battery to handle power spikes of this type will reduce the overall size of the fuel cell stack, but this solution adds to the overall size of the power pack and will again decrease practical energy density.

The single fuel cell can be considered the repeat unit for our fuel cell system rough analysis (see figure 2.2.1-1). The core unit is the fuel cell cathode-electrolyte-anode multilayer thin film. Assuming that electrolyte and electrode thicknesses range from 100 nm
to 1000 nm, the core unit thickness ranges from 300-3000 nm. Incorporation of both air channels and fuel channels will add significantly to the size of the core unit, with channels of about 200 microns wide by 50 microns high in cross sectional area [12]. These channels also act as the reaction chambers for the fuel cell. The substrate will account for most of the remaining thickness. The repeat unit can then be assumed to be approximately 500 microns thick. Area is variable and depends on the reliability of the freestanding electrode/electrolyte core unit. Thin film freestanding electrolytes with areas up to 500 microns by 500 microns have been reported [18].

![Diagram of SOFC](image)

**Figure 2.1.1-1 : One possible MEMS thin film solid oxide fuel cell design [12]**

With an array of cells on a substrate, each cell has an active area of 250,000 square microns (0.0025 cm$^2$) and a thickness of about 500 microns. Connection of cells can be performed using standard interconnect designs from the microelectronics industry to achieve either parallel or series connections between the cells to get the proper voltage and current output characteristics. Cell spacing is important in that it will affect the overall power density of the fuel cell ‘stack’. If we assume that cell spacing is about 100 microns, the repeat unit area rises to 360,000 square microns (about 0.0036 cm$^2$). The volume of a single repeat unit is then $1.8 \times 10^{-4}$ cubic centimeters. The relevant values are given in Table 2.1.1-1.
Power density is typically expressed in W/cm² for fuel cells, relating the power to the active area of the electrolyte. The highest reported power density for fuel cell stacks is just over 1 W/cm², from Lawrence Livermore National Laboratories [2]. While single cell power density has been reported up to 2 W/cm², stack power density is considered a more practical parameter for useful approximation. Using an average power density of 500 mW/cm², the single cell power output then becomes 1.25 mW for a 1.8 x 10⁻⁴ cc volume. Normalizing power to volumetric power density (W/cc), the fuel cell stack as a whole is capable of achieving about 7 W/cc. This is easily enough to power a standard mobile phone. For comparison, current Li-ion battery packs deliver 0.4 W/cc [7]. Size assumptions scale, so if a 1000 um thick repeat unit is assumed (twice as thick), volumetric power density drops to half, about 3.5 W/cc.

Packaging of the fuel cell stack will introduce more components and further increase the volume of the system, subsequently diluting the energy density. Assuming a seven watt one cubic centimeter chip can power a mobile phone, it must then be packaged and protected from the environment, including thermal insulation components, fuel and air delivery components (perhaps micro fans to control flow rate), and exhaust gas handling components (unutilized fuel and air, water vapor, and carbon dioxide). While estimation of these components’ volumes are difficult, a conservative estimate of the total packaging volume for a one cc fuel cell stack is perhaps 3 cc. Thus the entire system occupies about 4 cc volume. It should be mentioned that some of these components do not necessarily scale with the size of the stack. For example, one MEMS air blower may be sufficient to provide the flowrate necessary for a four cell stack, or a twenty cell stack. Thermal insulation around the periphery of the operating stack need not be duplicated within the stack. Packaging efficiency can be estimated by finding the ratio of the fuel cell system volume to the fuel storage volume. As an exercise, this method can be applied to a specific mobile phone.

A standard low profile mobile phone, the LG-TM510, uses a battery with a total volume of 29.5 cc (see Figure 2.1.1-2). Packaging efficiency can then be approximated by

<table>
<thead>
<tr>
<th>Stack dimensions</th>
<th>Area (um²)</th>
<th>Thickness (um)</th>
<th>Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 x 500</td>
<td>500</td>
<td>1.25 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Cell spacing</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total dimensions</td>
<td>600 x 600</td>
<td>1.80 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Power density</td>
<td>500 mW/cm²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>0.00125 W</td>
<td>1.80 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Specific power</td>
<td>6.94 W/cc</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
assuming an equivalently sized fuel cell system. With 4 cc taken up by the fuel cell stack and sub-components, the remaining volume can be used for fuel storage. The battery’s approximate profile is 73mm x 47mm x 8.6mm [19]. Allowing for a 2 mm wall in the fuel container and a 10mm x 47mm x 8.6mm volume for the fuel cell stack, the remaining volume is dedicated towards fuel storage – 59mm x 43mm x 4.6mm. The approximate fuel capacity drops to 11.7 cc. Packaging efficiency can be calculated as percent volume fuel, and thus the packaging efficiency is about 40% in this case. Using butane, the theoretical capacity is 7,700 Whr/L. Thus the fuel cell system in this case has a theoretical energy of 90 Whr. If the fuel cell system efficiency is 30%, then the useful energy from the system drops to 27 Whr. Thus the energy density can be calculated to be 915 Whr/L. This is about two and a half times higher than the quoted energy density values of standard lithium ion batteries at 350 Whr/L.

However, a more direct comparison can be made with the existing battery pack for this mobile phone. At a voltage of 3.7V, the fuel cell constitutes about 7.3 Ahr, or 7300 mA-hrs of capacity. The equivalently sized battery, however, contains only 900 mA-hrs [19]. This constitutes an increase in energy storage of 711%, or about eight times higher than the battery, a substantial increase. Of course, this is a rough estimate, but the potential for improvement is obvious. The assumptions of 30% system efficiency, 40% packaging efficiency, power density, and stack volume are conservative, and will improve as the technology is developed.

The profile of the battery being replaced has a significant impact on the energy density due to the packaging. Those shapes with large surface area to volume ratios, such as a typical slim-line battery design, will suffer from loss of fuel storage volume due to the fuel storage container itself. This appears problematic in that current battery technology is being driven by mobile phone manufacturers towards slimmer profiles. However, simple redesign of the fuel container to a shape with lower surface area to volume will increase the packaging efficiency and thus the overall energy density of the system. In addition, larger systems such as notebook...
computers will allow higher packaging efficiency in that the fuel cell stack and other components will remain at a constant size, while the volume available for fuel increases. Considering improvements in packaging efficiency to 75%, the final energy density of a butane fueled micro SOFC becomes approximately 1700 Whr/L. If micro-SOFC system efficiency approaches 50%, as it is in large scale applications, the final energy density then rises to about 2900 Whr/L. Wasted energy lost as heat is also reduced, as a 50% efficient fuel cell will produce much less waste heat than a 30% efficient fuel cell.

A simple additional calculation can be made to approximate the energy density of polymeric fuel cells for comparison as well. Due to the storage issues with hydrogen for portable applications, the majority of micro fuel cell efforts have been focused on the direct methanol fuel cell (DMFC). These fuel cells utilize a polymeric membrane as the electrolyte, and operate at substantially lower temperatures than solid oxide fuel cells. Direct methanol fuel cells, while using liquid methanol as a fuel, typically need dilution of the methanol with water for proper operation. Polymer membrane hydration is important for keeping the conductivity of the membrane high. Methanol is also corrosive to the membrane. This dilution can result in fuel mixtures with as little as 1% methanol or as high as 50% methanol, though most systems hover between 5% and 10%. Using a maximum methanol concentration of 50%, the energy density becomes 2,450 Whr/L. System efficiencies of DMFC’s can be as high as 30%, similar to current SOFC performance levels; however, the potential efficiency of the DMFC is much less than that of the SOFC due to a number of different factors including methanol crossover (direct oxidation of fuel by diffusion of the fuel through the electrolyte). Using an efficiency of 30%, the energy density drops to 735 Whr/L. Finally, assuming a packaging efficiency of even 80%, the energy density is still only 588 Whr/L, which, though twice as high as current lithium ion battery technology, is still much less than the potential energy density of micro solid oxide fuel cells.

In terms of mass, energy density (Whr/L) needs to be converted into specific energy (Whr/kg). Conversion of energy density to specific energy can be performed by estimating the physical density of the system. Higher physical density will of course result in a lower absolute value of specific energy as compared to energy density. Depending on the ultimate design, it is likely that the volume of the fuel cell will for the most part be comprised of fuel or external packaging (plastic). The stack itself utilizes high density materials (ZrC₂, CeO₂) as functional materials, and silicon as a substrate, but the small amounts of the actual materials used have a
negligible effect on the overall density of the system. In addition, the repeat units for the cells have a large volume of empty space in the form of channels or porosity (in the electrodes). As the fuel itself can have a low density (butane \( \sim 0.6 \text{ g/cc} \)), it is likely that the overall density of the system will be close to or less than 1 g/cc.

It is clear that, based on energy storage capacity, micro solid oxide fuel cells are immediately superior to lithium ion battery technology. With improvements in parameters such as system efficiency and subsequent increases in power density and packaging efficiency, micro solid oxide fuel cells may easily provide ten to twenty times the life of current lithium ion batteries.

2.1.2 Power Output

While energy density is the primary figure of merit for comparison of micro SOFC technology to battery technology, there are other areas that need to be evaluated and compared against. One of these is power handling. Fuel cells are typically unable to provide a constant level of power with varying loads. There is a peak power output that occurs due to the characteristic shape of the voltage-current plot, as previously discussed.

The voltage drops due to internal resistances of the fuel cell. Reducing these internal resistances (by thinning the electrolyte and/or increasing conductivity of components) will flatten the slope in the linear region of the plot. In Figure 2.1.2-1, a characteristic plot of fuel cell voltage vs. current density is shown. The fuel cell with higher ohmic resistance is shown as voltage. Power loss is clearly greater on this fuel cell. However, plot voltage has a lower ohmic resistance. This will result in higher power density and better overall handling of power requirements. Despite efforts to minimize this effect, there will always be a variable power output dependent on the load resistance, and a particular peak power output at a certain voltage output and current density. Thus as the load resistance changes, available power will also change. Designing the stack to handle these peak power loads can be accomplished, but at the expense of making the stack larger, effectively increasing the active area to achieve higher current and power.
Figure 2.1.2-1: Effect of ohmic resistance on voltage and power output of fuel cells; Voltage and Power curves are characteristic of a fuel cell with a lower ohmic resistance, while the Voltage' and Power' curves are characteristic of a fuel cell with higher ohmic resistance.

This is a clear disadvantage of fuel cells. Current designers in both the polymer electrolyte (PEMFC) and solid oxide (SOFC) type fuel cells are considering employing rechargeable batteries or other energy storage devices such as supercapacitors to handle large transient power demands, or by supplying the fuel cell solely for recharging the battery, which exclusively handles power.

Batteries, while handling high power demands better than fuel cells, do suffer from another drawback – self discharge. Batteries have a definite shelf life when not in use – lithium ion batteries can discharge at a rate of 10% per month, while a nickel metal hydride battery can discharge 30% in one month [20]. Fuel cells do not suffer from this drawback. Thus the advantage of fuel cells is clear in those applications that require intermittent power over long periods of time. Discharge rate is also strongly dependent on ambient temperature, which makes battery lifetime difficult to predict. Battery capacity is usually measured at room temperature – use of the battery at high temperatures will shorten its lifetime (laptop computers), while low temperatures will degrade performance. Solid oxide fuel cells operate uniformly at all ambient temperatures due to the relatively high stack temperature required. Thus they are more robust and predictable than batteries in this respect.
Most digital equipment today uses short intermittent bursts of power, also known as pulse discharge. High currents are required to power the device; for example, the GSM (Global System for Mobile communications) protocol for mobile phones requires up to 2.5A in 550μs pulses every 4.5 ms during talk (using a standard 3.6V single lithium ion cell). If a battery is rated at 1000 mAh, the 1C (capacity) discharge rate is 1 ampere. For most batteries, lifetime is measured at C/5 or 0.2C (in this case, 200 mA). Thus the pulse discharge rate for GSM protocol is 2C. Most lithium batteries are limited by self-protection circuitry to prevent discharge rates over 2C. Lifetime is shortened by high current bursts, down to about 80% nominal capacity for Li-ion batteries [20]. However, fuel cells, while unaffected by pulse discharge, may not even be able to handle high pulses of current and would require supplemental current through a secondary battery, supercapacitor, or other energy storage device.

2.1.3 Use Model

Another factor that can affect the success of micro fuel cells in the marketplace is the use model. The first use model factor deals with the recharging aspect. Currently, users are accustomed to plugging in a portable electronic device in a wall charger or car charger to replenish the power supply. This use model is essentially free of additional costs to the user since the electricity from the car or from the wall is not directly paid for. However, micro fuel cells must change the use model from recharging to refueling. The refuel will be almost instantaneous, while recharging from a discharged battery can take up to three hours; this is a clear advantage for fuel cells. But assuming the fuel will be stored and carried in a form of cartridge, perhaps similar to a butane cigarette lighter, users may balk at the idea of purchasing fuel cartridges to replenish the power supply, when before, they could recharge for free. In addition, to become truly mobile, the user would have to physically carry an extra fuel cartridge or cartridges, depending on the usage time needed (the analog of course, is carrying the appropriate battery charger). While this is perfectly satisfactory or decidedly superior to rechargeable batteries in outdoors environments such as camping, hiking, or military applications, in today’s world of ubiquitous electric outlets (to the common citizen), the refueling mode may be more of a hindrance than a convenience. Perception of a “return” to the primary battery use model (purchasing replacements for power) could be a disadvantage to the micro fuel cell. Cost and availability of the refuel cartridge will be the
key driver for this factor in the consumer markets. The widespread acceptance of micro fuel cells for consumer devices could be limited by this change in use model.

The second aspect is that the user’s expectation of a mobile device is limited power. Users are trained to carry extra batteries, recharge frequently, and conserve power by not using the device, if necessary. While this behavior is sufficient to mitigate the limits of current battery technology, it is certainly not desirable. For true mobility and effectiveness of the device, users should be able to use the device freely and as often as wanted, and not have to worry about sudden failure due to ambiguity of the state of charge of the battery. In addition, carrying chargers while traveling is often a hindrance, complete with tangled wires and searching for electrical outlets to plug into. Multiple charging stations make sense, but having a dedicated charger for home, office, and automobile adds to the overall cost to the consumer. Micro fuel cells are free from any separate charging device, and could easily provide accurate remaining power information by a simple fuel gauge. In that respect, the micro fuel cell could be seen as tremendously enabling to mobility.

The third use model factor deals with the fuel itself. Fuel, especially the concentrated hydrocarbon fuel that seems the best advantage of the solid oxide fuel cell over the polymer electrolyte fuel cell, is an inherently hazardous substance. In addition, portable electronic devices are used in airplanes, among other places. Allowing a person to carry fuel, perhaps moderate to large amounts as could be required for a fuel cell powered notebook computer, is currently prohibited. Relaxation of these laws would be required to allow flammable liquids onboard commercial aircraft, which is unlikely with today's safety precautions. However, there has been reported acceptance of diluted methanol fuel onboard aircraft [21] – which is typically used in the polymer electrolyte membrane fuel cells – due to the low level of methanol in the fuel, which is currently 24% methanol, 76% water.

These use model factors will undoubtedly have some impact on the market’s acceptance of micro fuel cells in general, and to date, there have been no published surveys or studies conducted to gauge the end user’s response to these changes in the fundamental use model for portable electronics [22]. As with many new or emerging technologies, the effect of these “softer” factors may have to wait until first products are introduced before their impact can be known.
2.1.4 Low power electronic/display technologies

The main problem micro fuel cells are trying to alleviate is power shortage. However, this problem can be approached from the standpoint of reduced power consumption. Low power electronics and display technologies are currently being developed to help alleviate the common problems associated with mobile electronics. Instead of increasing onboard energy storage to increase operating lifetime, some companies are designing electronics that consume less power to extend operating lifetime. Essentially, this approach is similar to designing a car that runs the same distance on less gas. Transmeta Corporation has developed new lower power microprocessors, using less than 1 watt of power, and are among the many companies currently developing mobile processors with efficiency in mind. Intel also has a low power consumption electronics initiative, recently releasing the Centrino® for mobile computing applications. These processors, consuming much less power, and utilizing technology to tailor power consumption to the computing demand on the fly, extend operating lifetimes by a factor of 2 to 4. In addition, lower power consumption leads to cooler electronics, which will aid in shrinking the overall size and weight of the application.

LED technology has also been improved to the point where the cost is within reach of many electronic device requirements. With a much higher lumens/watt output, they stand to greatly reduce the power required for producing light, thus increasing battery lifetimes significantly. In addition, organic and quantum dot LED technology, a burgeoning field, shows promise in producing high brightness, low power and low volume displays for a myriad of applications including portable devices.

While boosting power efficiency of the electronics is an elegant solution to the energy density problem, it does not necessarily preclude a place for micro fuel cells. Combination of low power electronics and displays with a micro fuel cell power system may enable a new breed of mobile electronics with incredibly long lifetimes (perhaps 40x operating life) and capability for uninterrupted mobile use.
2.2 Portable Electronics

Within the portable electronics sector, some devices are obvious targets for micro fuel cell technology. The largest consumer products include laptops and mobile phones. These two products represent the largest market for micro fuel cells. Notebook computer unit sales in 2002 were 4.4 million [23], and mobile phone handset unit sales were approximately 423 million [24]. The high price of laptop batteries, combined with their necessity for long continuous runtimes make this application very tantalizing for micro fuel cell manufacturers, while the attraction of the mobile phone handsets market is its large volume. Other devices represent significant opportunities as well, as PDA unit sales totaled 3.2 million units [25], while digital camera unit sales totaled 9.4 million units [26].

2.2.1 Military

Clearly, energy is becoming a more important aspect of today’s infantry soldier. As weapons and communications gear become more high-tech, the overall power requirements for the soldier increase dramatically. In one example, the Army’s $2 billion Land Warrior program seeks to increase the lethality, survivability, and command and control of the infantryman. One major problem with the project is power. Current batteries last only about 150 minutes with all systems running, and prototype batteries hope to push operating times up to 30 hrs [27]. In addition, weight is a key requirement. The total pack weight of the enhanced systems must be below 80 lbs.

The DARPA Palm Power program seeks to produce 20W power sources that are very small, lightweight, and rugged. Assuming an average power demand of 20W, mission parameters require a certain energy capacity and weight. Mission lengths up to ten days would require 4800 Whrs of power in a 1.6 kg pack, leading to an energy density requirement of 3000 Whrs/kg [28].

Current Army rechargeable lithium ion batteries are designated as BB-2590 and operate at either 12V or 24V. Typical specifications are given in Table 2.2.1-1 [29], and a comparison of ‘power supply’ weight for a 10 day, 4800 Whr mission using both batteries and a micro SOFC is given.
Table 2.2.1-1: Army battery specifications vs. potential micro SOFC

<table>
<thead>
<tr>
<th>Type</th>
<th>Wh/kg</th>
<th>Wh/L</th>
<th>Volume</th>
<th>Unit wt.</th>
<th>10 day mission wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-5590 (primary)</td>
<td>167</td>
<td>189</td>
<td>900 cc</td>
<td>1.02 kg</td>
<td>28.2 kg</td>
</tr>
<tr>
<td>BB-2590</td>
<td>200</td>
<td>231</td>
<td>883 cc</td>
<td>1.30 kg</td>
<td>24.0 kg</td>
</tr>
<tr>
<td>12V micro SOFC*</td>
<td>~1900</td>
<td>~1700</td>
<td>900 cc</td>
<td>0.8 kg</td>
<td>2.5 kg</td>
</tr>
</tbody>
</table>

*Estimated values

Utilizing a 12V micro solid oxide fuel cell in the same volume as required by the specifications, and following the previous rough model using 30% system efficiency the approximate energy density and specific energy can be calculated. Specifications for the BB-2590 military rechargeable lithium ion battery [37] state the dimensions to be 11.18 cm x 12.7 cm x 6.22 cm with a peak power output of 50W. Using the previous assumption of 10W/cc, the total stack volume becomes 5cc. Allowing 15cc for other stack components, the remaining volume can be devoted to fuel storage. This leads to total fuel capacity of 675 cc (assuming a 4 mm fuel tank wall thickness). Packaging efficiency is then calculated to be 76%. The overall energy density is then about 1700 Whr/L. If the average physical density of the system is 0.9 g/cc, the specific energy is calculated to be about 1900 Whr/kg. This is a marked improvement over conventional batteries and places the goals set by Palm Power of 3000 Whr/kg within reach, though further refinement of the technology is still needed. The challenges to this application are the need for ruggedness and extremely high reliability. Mechanical shock-proofing, waterproofing, and vibration survival are all requirements for the military. These are likely to increase the packaging requirements and thus lower the energy density.

Self-discharge is a current problem for batteries. Shelf life is a problem and is a source of logistical problems for the military supply room. State of charge is another problem in that it is difficult to determine how much charge is left on a battery [30]. With fuel cells, this is not a problem. Fuel gauges can easily meter the amount of energy remaining in the fuel reservoir, and fuel cells do not self-discharge.

It is prudent to seriously consider the military market as the best near term application. US based companies may have a slight advantage in this area due to government funding that is largely unavailable to foreign companies. There is also a clear and present need for high energy dense devices to power leading edge military technology for soldiers. In terms of energy density, micro fuel cells are a leading candidate for soldier portable power.
2.2.2 Consumer

Consumer applications present a large variety of mobile devices. Most devices fall in one of the categories of computing, communications, or entertainment. As stated before, the largest opportunities for micro fuel cells lie in the product applications of mobile phones and notebook computers. The high prices of the batteries currently being used in notebook computers and the sheer volume of mobile phones combined with handset turnover rate drive these two areas.

The use of micro fuel cells in mobile phones has been highly publicized. The impact that fuel cells could have on mobile phones is huge. Longer standby and talk times, perhaps on the order of eight to ten times that provided by today’s battery technology, would change the use of mobile phones in the short term and also irreversibly impact design of new mobile phones in the long term. The ubiquity of the mobile phone in modern society would introduce the micro fuel cell as a viable alternative to batteries, raise mainstream awareness of the device, and spread to other areas would be inevitable. Depending on the profile of the phone, the micro fuel cell could have energy densities up to ten times that of standard rechargeable batteries, resulting in standby times of one month or more, and talk times of over fifty hours. When the fuel is depleted, simple insertion of a new fuel cartridge would allow the user to continue using the phone without searching for a charger or wall socket. However, ultra slimline phones with thin battery profiles will result in lower packaging efficiency for micro fuel cells – which is not a problem for prismatic or lithium-polymer batteries. Redesign of the phone to accept optimal micro fuel cell shape factors will help to alleviate this problem, but partnering with handset manufacturers may be difficult.

Notebook computers present a larger battery profile than mobile phones and thus packaging efficiency is likely to be much higher. Again, with energy densities up to ten times that of batteries, operating times of 30 to 40 hours could be realized, with instant refuel capability and no need to stay tethered to a wall for an hour or so to recharge the battery.

However, the use model changes impose a different set of constraints on the probable acceptance of micro fuel cells in the consumer marketplace. The initial cost of the micro fuel cell is likely to be much higher than the current rechargeable battery in the near term. Add the cost of the refuel cartridges and the final cost to the consumer increases once again. With these barriers to entry, mainstream consumers may find it difficult to justify purchasing these devices to power their electronics. Indeed, the most likely early adopters might be so-called
'road warriors'—those whose livelihood depend on computing and communications mobility (e.g. high power executives or sales and marketing professionals). Yet these users are trained to recharge their devices every evening, and have found ways to cope with the limited energy density of their devices. They also constitute only a small fraction of the total available market, and thus would likely be insufficient to support short term revenue goals.

Large consumer electronics manufacturers are more likely to partner with established battery companies in the design of next generation devices. As the design of the portable electronic device is largely constrained by the power available to it, prior knowledge of the limitation of the available power source is absolutely necessary and will dictate the functionality of the device. Design of a new device that takes advantage of the micro fuel cells' much higher energy density could be more likely to go forward with an established battery manufacturer's version of the micro fuel cell than with a startup company's version.

There are some specialty applications in the consumer area that could benefit from micro solid oxide fuel cells though. Video equipment is an application where both power consumption and low weight is desired. Power drain on devices such as digital cameras with flash and bright LCD displays is enough of a problem to warrant special alkaline batteries for high drain devices from manufacturers such as Duracell and Energizer. Camcorders typically do not include on board lighting of any sufficiency due to the problem of power consumption. For digital imaging devices, new applications could exist in terms of brighter on-board lighting and brighter displays. For these devices, batteries would not be sufficient and fuel cells could be the only viable alternative. An even greater need exists in the professional or semi-professional video equipment market. As video equipment becomes more advanced and smaller, more and more video productions are being shot with small portable high-end cameras due to convenience. However, the lighting requirement for pro and semi-pro production is very high. Lighting is the primary drain on power, and even with higher efficiency lighting like LED's, power consumption is still a problem. Battery packs are heavy and lifetime is inadequate. The issue is most readily apparent when shooting on location. In fact, there is an entire industry built around battery vests and belts to allow the user to comfortably carry sufficient power for the job. The energy densities available for these applications are still very low. A small sampling of batteries available for these applications is shown in table 2.2.2-1.
Table 2.2.2-1: Battery specifications for video equipment

<table>
<thead>
<tr>
<th>Battery</th>
<th>Watt-hours</th>
<th>Price/Whr</th>
<th>Volume</th>
<th>Weight</th>
<th>Specific energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIONIC 80</td>
<td>80</td>
<td>$5.63</td>
<td>640 cc</td>
<td>773 g</td>
<td>104 Whr/kg</td>
</tr>
<tr>
<td>IDX E-50</td>
<td>48</td>
<td>$5.42</td>
<td>398 cc</td>
<td>520 g</td>
<td>92 Whr/kg</td>
</tr>
<tr>
<td>IDX E-80</td>
<td>82</td>
<td>$5.24</td>
<td>711 cc</td>
<td>735 g</td>
<td>112 Whr/kg</td>
</tr>
<tr>
<td>NiCd Belt</td>
<td>120</td>
<td>$4.12</td>
<td>392 cc</td>
<td>1250 g</td>
<td>27 Whr/kg</td>
</tr>
</tbody>
</table>

Thus it is likely that for near term goals, the small micro fuel cell startup company should concentrate on military or specialty applications, and develop the technology to the point where it becomes attractive to larger established companies. Projection of IP during the development process is critical.

2.3 New Applications

New applications are the other broad category of uses for the micro solid oxide fuel cell. These are applications that are either enabled by micro fuel cells or have not been developed yet, and represent the undefined space for mobile electronics. This area is necessarily hard to analyze or predict, and Christensen [31] supports this, saying:

Markets that do not exist cannot be analyzed, suppliers and customers must discover them together. [p. 165]

Despite this, a general trend can be envisioned at this point. Micro fuel cells' higher energy density can enable new breeds of electronic devices that are unavailable with current battery performance. Combinations of power hungry mobile applications such as Wi-Fi or multimedia push the limits of battery technology [32]. Next generation smart phones that combine digital cameras, speakerphone, digital music, and wireless data connectivity already exist today. Taking these applications one step further may represent one possible avenue for new applications.

Work being done at MIT Media Lab in ‘wearable computing’ is one such application that could be enabled by micro fuel cell technology. The power requirements of integrating multiple pieces of hardware into a wearable harness necessitate a large battery pack. Consolidating all the power requirements such that they could be fulfilled by a micro fuel cell system would lighten the harness and could also allow more functionality to be integrated into the system.
A new class of applications that combine fuel cells and rechargeable batteries is emerging today. These applications are basically fuel cell based chargers for batteries that operate while the electronic device is not in use. It combines the power handling performance of a battery with the energy density of a fuel cell. Current applications of this idea are bulky however, and further refinement is necessary.

New applications are necessarily a longer term proposition for companies to pursue, especially for startups. Existing applications have a defined boundary and an established set of requirements, and thus offer some predictability in earning revenue in the short term. New applications, being inherently vague, present a problem and are best tackled when the company’s revenue stream is more established.

2.4 Market Penetration

Success of the micro fuel cell in the battery market is still unclear. An argument to qualify and predict the penetration of a new technology into an existing market can be made by viewing micro fuel cell technology as either a sustaining technology or a disruptive technology [31]. In every field there exist technology improvements that increase performance. In many areas, the performance can be measured and even predicted. A prominent example is Moore’s Law in the semiconductor industry. Sustaining technology is defined as those improvements that maintain the pace of improvement, following customer demands. This exists to some extent in the battery market as well. Improvements in battery materials and designs have led to today’s standard Li-ion batteries, with energy densities of about 350 Whr/L. It has been predicted that the energy density will continue to improve, but at a slower rate, and eventually taper off (see figure 2.4-1).
Figure 2.4-1: Li-ion battery development by year [7]

Thus a new sustaining technology will be needed to pick up where Li-ion leaves off. The other type of technology, disruptive technology, does not follow the improvement, but instead, it actually underperforms the existing technology at first, usually in niche markets where other aspects of the technology are desired (smaller, convenient, cheaper). Over time, the disruptive technologies tend to improve due to their own ‘sustaining’ technology advances, and eventually are able to overtake the ‘established’ technology in its home market. Some examples of disruptive technology are given in Table 2.4-1.

Figure 2.4-2: Disruptive vs. sustaining technology [31]
Micro fuel cells can be characterized as one of these technologies due to their operating characteristics and improvements. In the battery market, the desired features are: low cost, long operating lifetime, and low weight. In addition, the power supplied to the device must be able to handle variations in power demand, with the acceptance that the voltage of the battery over time will diminish as the charge is depleted. The absolute size or volume of a micro fuel cell is potentially much less than that of an equivalent battery. A stack using electrolytes of 500nm thickness, electrodes of 1um thickness, and interconnects of 10um thickness can be made very tiny indeed. Depending on power requirements, the fuel cell may be able to be integrated directly into the electronics of the device. The remaining volume can be dedicated to fuel storage – which can be designed separately from the fuel cell, allowing increased design flexibility. The energy density of the fuel cell will be much higher than that of an equivalent size battery, and recharging will not be needed as often. This makes the micro fuel cell much more convenient to use. Finally, using silicon manufacturing technology, it is likely that the high volume/low cost paradigm that constantly pushes the price of electronics down while increasing its performance will have a similar effect on micro fuel cells, making them cheaper than batteries. These factors; small size, convenience, and low price, indicate that micro fuel cells could initially be considered a disruptive technology.

<table>
<thead>
<tr>
<th>Established Technology</th>
<th>Disruptive Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver halide photography</td>
<td>Digital photography</td>
</tr>
<tr>
<td>Wireline telephony</td>
<td>Mobile telephony</td>
</tr>
<tr>
<td>Medical doctors</td>
<td>Nurse practitioners</td>
</tr>
</tbody>
</table>

Looking again, we can approach this characterization from another direction. Comparing micro fuel cells to batteries, we can easily see that the cost will be higher at first, that the lifetime will be longer, and that the weight will also be lower, thanks to improvements in energy density. The micro fuel cell will clearly deliver the increase in performance required to maintain the improvements seen in the industry. It appears that micro fuel cells can also be considered a sustaining technology in a sense that the improvements stay within the inherent value network of the rechargeable battery realm. In other words, the factors that make one battery better than the next – higher energy capacity, lightness, small size, and low cost – are the exact same factors that micro fuel cells will
capitalize on in their efforts to displace battery technology. While this sustaining innovation is radically different from previous evolutions in rechargeable battery technology – from nickel cadmium to nickel metal hydride, and then to lithium ion – it better fits the sustaining innovation profile and could be considered a ‘radical’ sustaining innovation.

Characterizing the micro fuel cell as a sustaining technology has impact on how the technology will be introduced in the marketplace. Typically, the leaders in the market will adeptly identify, research, and develop sustaining technologies since it falls directly in line with their current customer demands. Large rechargeable battery companies would then be expected to be developing micro fuel cells as a way to increase their market share and competitiveness, and their financial stability and resources almost ensure their success over small startup companies in the same area. The major rechargeable battery manufacturers are either Japanese or Korean (Sony, Panasonic, Toshiba, Sanyo), and all have fuel cell development programs underway. Little information is available for these programs, but the information that is available characterizes them as direct methanol fuel cell programs using a polymer electrolyte design. Startup companies are at a disadvantage in that there is no large financial resource to back development or marketing costs – and have to rely solely on venture capital or other short term financing. One strategy for small startups is to pursue federal grant money since the government wants to bring some of that market back to the United States. Since the three big rechargeable battery makers are Japanese, and the market is expected to grow substantially, the idea is the government has a vested interest in keeping the country competitive in this area. Another strategy is to pursue applications that are traditionally funded by the government, typically DOE, DOD, or DARPA. In addition to improving the country’s competitiveness in the commercial sector, US-based startups can develop specifically for military applications and have access to funds that are unavailable to the large Japanese battery manufacturers.
3. Intellectual Property Landscape

Fuel cells are a well covered intellectual property area, partly due to the age of the field. A search on fuel cells listed close to 6000 patents related to the art. “Solid oxide fuel cell” produced 356 patents. Micro fuel cells or thin film fuel cells also produced patent matches. A search using the terms “micro”, “miniature”, “thin film”, and “silicon” on all fuel cell related patents revealed 180 matches. Most of these patents, however, deal exclusively with PEMFC, or polymer type fuel cells. These will invariably state ‘cations exchange’ membranes or ‘polymer electrolyte’ in the body of the claims and should have no blocking impact on the development of micro solid oxide fuel cells.

In the realm of microfabricated solid oxide fuel cells, there are few competitors. The technical challenges of high temperature operation in a portable electronic device are high, and few organizations have attempted to create a viable product. There are a number of patents that are relevant to the art, however. This section will list the US patent positions held by various entities.

There are some early patents with relevance to the technology in the area of solid oxide fuel cells. The first of these is US patent 5,641,585, filed on March 21, 1995 and issued on June 24, 1997, invented by Paul A. Lessing and Anthony C. Zupero at Lockheed Idaho Technologies Company [33]. The first claim states:

1. A self-contained power source assembly for use in providing electricity, the power source assembly comprising:
   a plurality of fuel cells connected in series, each fuel cell having an anode, a cathode, and electrolyte for producing electricity by oxidation of supplied fuel;
   fuel source means for supplying fuel to the fuel cells;
   first routing means for directing flow of fuel about the anode of the fuel cells;
   second routing means for directing the flow of air about the cathode of the fuel cells;
   air pump means for moving air about the fuel cells adequate to produce a desired power output;
   catalyst means for reforming the fuel into the chemical components needed for oxidation; and
   electric starter means for adding heat to the system thereby to initiate oxidation.
This claim is very broad and uses open ended language, claiming any self-contained power source assembly for providing electricity that contains a fuel cell stack. Connection in series is specified, while parallel connection is not claimed. Furthermore, means to supply fuel and air (including an air pump) to the appropriate locations, a catalyst, and an electric starter are disclosed. Indeed, this claim covers the type of micro solid oxide fuel cell assembly being proposed. This patent further discloses within the body an example for use within a cellular phone, laptop, or other portable electronic device. While the assignee of this patent is Lockheed Idaho Technologies Company, the United States government also has rights to this patent under a previous contract with Lockheed Idaho. From a cursory search, it does not appear that Lockheed Idaho is pursuing any commercialization of the device disclosed in its patent, nor are the inventors furthering the work described.

Intellectual property positions are also held by The Regents of the University of California, the operators of Lawrence Livermore National Laboratories. The United States government also has rights to these patents. US patents 5,753,385 and 6,007,683, both titled "Hybrid Deposition of Thin Film Solid Oxide Fuel Cells and Electrolyzers", cover solid oxide fuel cells using cermet electrodes with either Ni, Fe, Co, or Co-Fe alloys for the anode, and Ag, Pt, or Pd metal for the cathode. The patents teach a thin film electrolyte (less than 10 um) and electrodes (between 1 and 750 um) for reduced ohmic polarization. They go into some detail regarding fabrication of such a SOFC, but do not explicitly discuss application of the invention in portable electronics.

<table>
<thead>
<tr>
<th>Patent</th>
<th>File date</th>
<th>Basic claim</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,007,683</td>
<td>Jul. 22 1997</td>
<td>The method of making the solid oxide fuel cell described in 5,753,385, using planar magnetron sputtering.</td>
</tr>
</tbody>
</table>

Claim 1 of patent 5,753,385 states [34]:

A solid oxide fuel cell comprising:
an electrolyte layer consisting of an ion conducting oxide;
a first porous electrode positioned adjacent one surface of said electrolyte layer and consisting of material selected from the group consisting of yttria stabilized zirconia and other material that matches the coefficient of thermal expansion (CTE) of the electrolyte, coated with a material selected from the group consisting of silver, platinum or palladium;
a second porous electrode positioned adjacent another surface of said electrolyte layer and consisting of material selected from the group consisting of yttria stabilized zirconia and other material that matches the CTE of the electrolyte, coated with a material selected from the group consisting of nickel, iron, cobalt, and Co-Fe alloys; and said porous electrodes having surfaces defining electrolyte-electrode interfaces located intermediate the electrolyte layer and said porous electrodes and consisting of material selected from the group consisting of yttria stabilized zirconia, and CeO.

It appears that the electrodes must be porous and also contain certain catalytic metals as stated in the claim. The patent background discusses the advantages of thin-film SOFC versus traditionally fabricated SOFC, and the fundamental problem of depositing cermets of yttria stabilized zirconia and metal in a porous layer. Patent 6,007,683 discusses the method by which this layer can be created, disclosing a planar magnetron sputtering technique. Claim 1 of patent 6,007,683 states [35]:

A method for forming a thin film solid oxide fuel cell, comprising:
forming an electrolyte from an ion conducting oxide by sputter deposition using a planar magnetron;
forming a pair of electrodes having a porosity of about 55%-25% by sputter deposition using a planar magnetron from a powder material composed of Y stabilized ZrO2 coated by a metal composed of Ag, Pt, Pd, Ni, Co, or Fe and sintered to form a porous compact;
forming electrolyte-electrode interfaces composed of a material selected from the group of Y stabilized ZrO2, and CeO2 on said electrodes by chemical vapor deposition so as to form a dense, smooth surface on the electrodes; and bonding the pair of electrodes to the electrolyte via the interfaces.

Thus the patent covers using sputter deposition to create thin film electrolytes and electrodes for SOFC, using specific target types, and forming an interface between the electrode and electrolyte by CVD for bonding the two components. Claim 2 of this patent is an independent claim, disclosing a similar technique as claim 1 but additionally imposing a metal content of less than 15% in the electrode, and applying the technique to a continuous deposition process which forms the first electrode, electrolyte, and second electrode in the same process, so as to
create stacks of fuel cells. It is known that a small MIT startup company outside Boston called Lilliputian Systems is granted exclusive license to the patents from Lawrence Livermore.

There are a series of patents issued to Northwestern University, Evanston, IL related to thin-film SOFC. Patents from this group are listed in Table 3-2.

<table>
<thead>
<tr>
<th>Patent</th>
<th>File date</th>
<th>Basic claim</th>
</tr>
</thead>
<tbody>
<tr>
<td>6,479,178</td>
<td>Apr. 10 2001</td>
<td>Planar fuel cells arrayed on a substrate interconnected together, using an anode with a catalytically active metal.</td>
</tr>
<tr>
<td>6,214,485</td>
<td>Nov. 16 1999</td>
<td>Direct oxidation of hydrocarbon fuel on a solid oxide fuel cell with no reforming step.</td>
</tr>
<tr>
<td>6,004,696</td>
<td>Mar. 22 1995</td>
<td>Silver-perovskite air electrode for a thin film solid oxide fuel cell</td>
</tr>
<tr>
<td>5,770,327</td>
<td>Aug. 15 1997</td>
<td>SOFC stack with a particular design – rectangular interconnects with three elongated cavities, fuel cell in between interconnects.</td>
</tr>
<tr>
<td>5,741,406</td>
<td>Apr. 2 1996</td>
<td>Method of making dense yttria-stabilized zirconia electrolyte 2 to 20 um thickness by sputtering zirconia and yttria targets.</td>
</tr>
<tr>
<td>5,656,387</td>
<td>Dec. 19 1995</td>
<td>Thin film SOFC with Ni-YSZ anode with grain size of less than 100nm, and Ni content between 30 vol% to 60 vol%.</td>
</tr>
<tr>
<td>5,395,704</td>
<td>Nov. 19 1992</td>
<td>Thin film SOFC with YSZ electrolyte, Ni-YSZ anode, and Ag-YSZ cathode</td>
</tr>
</tbody>
</table>

These patents cover related methods of producing thin film solid oxide fuel cells. Patent 5,395,704 teaches a standard thin-film solid oxide fuel cell, specifying Ni-YSZ for the anode and Ag YSZ for the cathode. Patent 5,656,387 teaches a thin film SOFC with an improved anode material – nickel-zirconia cermet with a grain size less than 100 nm to improve triple phase boundary area. Patent 5,741,406 claims a method for making a thin film SOFC using sputtering. An LSM substrate is used under 75-150V DC bias. First a YSZ electrolyte film is sputtered onto the substrate, followed by a fuel electrode. Subsequent claims narrow the scope of the patent to electrolytes greater than 2 um and less than 20 um, and using a Ni-Zr-Y target for sputtering the fuel electrode. Patent 5,770,327 teaches fabrication of interconnects from inexpensive metals and an uncomplicated assembly of a fuel cell stack. The rectangular interconnect contains three elongated cavities parallel to each other. The outer two cavities have a series of holes that open to the bottom of the interconnect, while the center cavity has a series of holes that open to the top of the interconnect. The cathode is placed on top of this interconnect, then the electrolyte, and finally the anode. Patent 6,004,696 covers silver-perovskite materials for air electrodes, teaching various compositions for such electrodes and preferred thicknesses between 0.5 um and 150 um. Patent 6,214,485 claims a method of directly oxidizing hydrocarbon fuels by using another improved cermet anode composed of a catalytic metal (Pt, Ru, Pd, Fe, Co, or Ni) and ceria. Finally, patent 6,479,178 teaches an array
of fuel cells on a substrate with various interconnect schemes, focusing on an anode containing a catalytically active metal for direct oxidation of a hydrocarbon fuel.

Claim 1 of 5,395,704 states [36]:

1. A fuel cell comprising:
   a yttria-stabilized zirconia electrolyte;
   a cermet fuel electrode comprising a yttria-stabilized zirconia on and in intimate contact with one side of said electrolyte; and
   a cermet air electrode on and in intimate contact with the other side of the electrolyte, the air electrode cermet having the nominal formula Ag$_{1-f}$YSZ$_f$, where $f$ is volume fraction and ranges from about 0.5 to about 0.95.

Claim 2 goes on to state:

2. A fuel cell as defined in claim 1 in which the electrolyte and the fuel and air electrodes are thin films.

This is a relatively broad claim that covers standard solid oxide fuel cells in a thin film design that use yttria-stabilized zirconia as the electrolyte and the anode, but specifically states Ag-YSZ cermet for the cathode (5 vol% to 50 vol% Ag). The next patents of interest are 6,214,485 and 6,479,178. Both titled “Direct Hydrocarbon Fuel Cells”, these patents claim metal-ceria anodes and direct oxidation of hydrocarbon fuels without any reforming step using water or carbon dioxide. Claim 1 of 6,214,485 states [9]:

1. A method of using a solid oxide fuel cell for direct hydrocarbon oxidation, said method comprising:
   providing a catalytic metal anode and a ceria material contacting said anode; and
   introducing a hydrocarbon fuel to said cell, said fuel absent at least one of sufficient carbon dioxide and water sufficient to convert said hydrocarbon fuel to hydrogen, said method absent a hydrocarbon reforming stage.

US Patent 6,479,178 is a continuation-in-part of the previous patent. Claims 1 and 2 of 6,479,178 state [38]:

1. A solid oxide fuel cell assembly, comprising:
a substantially planar array of fuel cells on a substrate, each
said cell comprising cathode, anode, electrolyte and
electrode interconnect component structures, each said
component structure of each said cell having a sub-planar
arrangement of one said component structure to another;
an oxidant cavity adjacent said substrate; and
a fuel cavity adjacent said sub-planar anode arrangement.
2. The assembly of claim 1 wherein said anode comprises a
composite having a catalytic metal and a ceria material, said
metal present in an amount less than 60 weight percent of said
anode.

These claims are both broad and open-ended, claiming many aspects of micro-fabricated solid
oxide fuel cells. In essence, Claim 1 of 6,479,178 covers planar arrays of fuel cells on any
substrate that is indicative of thin films processing. Claim 1 of 6,214,485 claims direct
oxidation of hydrocarbon fuels on the fuel cell using a ceria based cermet anode, which is the
method of fuel oxidation preferred for the solid oxide fuel cell. Dr. Barnett’s work in thin-film
solid oxide fuel cells is extensive, and the intellectual property covers large areas of this field,
though application to portable electronics devices is not addressed in any way in the body of
the patents.

There are also patent applications with relevance to the area. One patent application is
from Lawrence Livermore National Laboratories, US patent application 2003/0039874,
published on Feb. 27, 2003. This patent application, titled “MEMS-based thin-film fuel cells”,
claim fuel cells fabricated using MEMS techniques. Claim 1 states [12]:

1. A fuel cell, including:
a fuel cell stack having an electrolyte composed of material
selected from the group consisting of solid oxide, solid
polymer, and proton exchange membrane materials,
means for supplying fuel and an oxidant to opposite sides of
said fuel cell stack, and means for heating said fuel cell
stack,
said means for heating includes a resistive heater,
said fuel cell stack including at least a pair of electrodes, and
an electrolyte separating said electrodes,
said electrolyte having a thickness of 0.5-50 μm,
said means for supplying fuel and oxidant including at least
one substrate having a manifold formed therein,
said manifold directing fuel to one side of said fuel cell stack.
This claim specifies thickness of the electrolyte as between 0.5 and 50 μm and limits the scope of the claims. However, the claim on a means for heating the stack is very broad and could include resistive heaters or any other heating means. The second independent claim of the patent application is claim 16:

16. A miniature thin-film fuel cell, comprising:
   a fuel cell stack including a pair of electrodes and an electrolyte layer, selected from the group consisting of solid oxides, solid polymers, and proton exchange membrane materials,
   a resistive heater for heating said fuel cell stack,
   a first substrate having an opening therein located adjacent said fuel cell stack,
   a second substrate having at least a fuel inlet therein secured to said first substrate and,
   a resistive heating means located in said fuel cell stack for at least said electrolyte,
   said electrolyte having a thickness of 0.5 to 50 μm.

This claim is similar to the first except that it applies to a miniature thin-film fuel cell, presumably for application towards portable electronic devices.

The second patent application of interest originates from Hewlett-Packard. This patent application, US 2002/0155335, published on Oct. 24, 2002, is titled “Hybrid Thin Film/Thick Film Solid Oxide Fuel Cell and Method of Manufacturing the Same” [39]. Claim one states:

1. A fuel cell, comprising:
   a thin film electrolyte layer having a first surface and a second surface, the first surface being opposed to the second surface.
   a thick film anode layer disposed on the first surface; and
   a thick film cathode layer disposed on the second surface.

This claim is effectively broad enough to cover most thin-film fuel cells. The patent teaches also the application of thin-film fuel cells not only to portable electronics, but also to energy storage devices connected to the electronics, which is made clear in claim 38:

38. The fuel cell as defined in claim 37, further comprising a material for connecting the fuel cell to at least one of an electrical load and an electrical storage device, the connecting material deposited on at least one of the anode layer and the
cathode layer, wherein the electrical load comprises at least one of computers, portable electronic appliances, and communication devices, and wherein the electrical storage device comprises at least one of capacitors, batteries, and power conditioning devices.

The patent also claims the method of manufacturing a thin-film solid oxide fuel cell. Claim 42 states:

42. A method of making a fuel cell, the method comprising the steps of:
creating a well in a dielectric or semiconductor substrate, the substrate having a first side and a second side, the second side opposed to the first side, and the well being defined in the first side;
depositing a thin film solid oxide electrolyte layer on the surface of the well;
applying an electrode layer in the electrolyte coated well;
creating a counter well in the second side, the counter well abutting the electrolyte layer; and
applying a counter electrode layer in the counter well.

With a total of 76 claims, this patent application seeks to cover much ground, but is based on the fact that thick film electrodes are used instead of thin film electrodes. The higher surface area of a thick film electrode is the driving force behind the teaching of thick film over thin film.

Thus, there is substantial intellectual property that needs to be addressed to ensure freedom to practice. Patentability of new developments is always open, however, and cross-licensing of any intellectual property granted during technical development of the micro SOFC will be invaluable. Being that there are still many technical challenges to overcome before the technology is viable for the market, opportunities exist for patentable innovations. Thermal management is a large challenge for micro SOFC as discussed before. Improvement of efficiency is another. To make a viable micro SOFC product for portable electronics applications requires hurdling these challenges, and patent protection on the solutions to these problems present opportunities for cross-licensing with the organizations holding the blocking intellectual property. Strong patent counsel is required to navigate the nuances of intellectual property issues, and should be utilized as early as possible to prevent the possibility of litigation.
3.1 Companies

There are few companies attempting micro solid oxide fuel cell technology, due to the technical challenges involved. One notable company is Lilliputian Systems, Inc., an MIT startup established in 2001, based in Woburn, MA. Using technology licensed from Lawrence Livermore National Laboratories and MIT, and its proprietary advances in solid oxide fuel cell technology, Lilliputian Systems hopes to enter the portable power market serving both military and consumer applications. In addition, MIT has its own research program funded by the US Army in creating micro-fabricated solid oxide fuel cells.

Another organization with an effort in small solid oxide fuel cells for portable electronics equipment is Alberta Research Council in Edmonton, Canada. Alberta Research Council (ARC) is developing the design and manufacturing processes for a tubular, anode-supported micro solid oxide fuel cell. With claims of up to 7.5W/cc, ARC plans to use the technology to enter the portable and transportation markets. A small scientific team of 5 researchers and one commercial analyst is working on the project, which started in 2001 [40,41]. ARC has five patent applications on its micro-SOFC design.

Hewlett-Packard has a published patent application in the field of micro-fabricated solid oxide fuel cells but there is little additional information on further developments. Hewlett-Packard’s site in Corvallis, Oregon is the likely source of the work being done in the field.

Development of micro-SOFC is limited, as only three companies are practicing in the area. However, development of micro-PEMFC is decidedly more active. There are many companies working in this area due to the technology’s lower operating temperature, lack of reforming need, and ease of processing. Many companies have joint development programs. A brief overview of the companies involved in the polymeric micro fuel cells approach is given.

Japanese firms have programs to develop micro fuel cells. Of prime interest are not only the consumer electronics manufacturers, but also the rechargeable battery manufacturers, as they have experience in the market space and are well positioned to take advantage of new applications in portable electronics, having served the market for many years. Casio has received press for publicizing its version of a direct methanol fuel cell integrated into a laptop computer, running a proprietary micro methanol reformer, and lasting
over twenty hours. Toshiba has also recently publicized a laptop powered by a fuel cell [42]. Samsung and Sanyo have entered a partnership to develop fuel cells, mainly for residential, stationary power applications, but have efforts to develop smaller fuel cells for portable electronics applications as well. Sony and Panasonic have programs in direct methanol, revealing in August 2001 a technology using fullerenes as the conductor for their fuel cell. Sony Frontier Science Labs has used this technology to develop a credit-card sized solid polymer fuel cell that can generate 1.2V of electricity without water vapor [43]. NEC Corporation is basing their PEM fuel cell technology on a carbon nanohorn.

Angstrom Power, Inc., is a Vancouver based company working on development of micro-structured PEM fuel cells, using micro-fabrication techniques to maximize efficiency and power density. It is based on technology developed at the University of Victoria by Gerard McLean, and is funded by Arete Corporation, Chrysalix Energy Limited Partnership, Growthworks, Ontario Power Generation, and Ventures West.

Jadoo Power Systems, based in Folsom, CA, is developing and marketing PEM fuel cell power solutions for surveillance applications and broadcast cameras, two areas where power is a severe limiting factor. Their product, the SuREII, provides six times the energy of existing battery systems for surveillance systems. The NABII unit, geared for professional video cameras, provides a similar improvement. Power is stored as a hydride with a specific energy of about 390 Wh/kg.

Energy Related Devices, a subsidiary of Manhattan Scientifics, is a developer of DMFC technology and seeks to capture the portable power market for pagers and cellphones. It is developing a cell phone charger in the form of a holster which the user can wear for market entry. Power density is 80 mW/cm² based on the latest reports from the company in April 2002 [44].

Medis Technologies is developing direct liquid methanol fuel cells that do not require a proton exchange membrane, but instead uses a liquid electrolyte. Through Medis' subsidiary More Energy, formed in Yehud, Israel in 1998, Medis is attempting to develop power packs for various laptops and cellphones.

Motorola Labs is researching direct methanol fuel cells to power portable electronics while they are in standby mode, and can recharge the battery at the same time. During use, the battery will handle peak power requirements. Using a multi-layer ceramic process,
Motorola’s technology integrates many different functions of the DMFC into two layers, simplifying the design.

MTI Micro Fuel Cells is a subsidiary of Mechanical Technology Inc., and has been very prominent in the micro fuel cell field. Working on its own version of a direct methanol fuel cell, MTI has shown prototypes in various stages of progress, powering cell phones and PDA’s, albeit in an “off-board” mode. Fuel delivery systems have been advanced to the point where fuel can be delivered without pumps and can work in any orientation. MTI is targeting mass market entry in 2004 for next generation mobile phone applications. MTI hopes to develop micro fuel cells for mobile computing equipment with Intermec and military radios with Harris Corporation. A partnership with Dupont to accelerate micro fuel cell development based on Dupont’s Nafion membrane was established in 2001.

Neah Power, a startup founded in 1999, has a patented technology for direct methanol fuel cells using a porous silicon substrate to increase power density. This technology also relies on a liquid electrolyte, thus eliminating the polymer membrane and bypassing the methanol crossover problem. Based in Bothell, Washington, Neah Power has backing from Intel, Alta Partners, and Frazier Technology Ventures. There are at least three published patent applications by Neah Power.

PolyFuel Inc., a spin off of SRI International based in Menlo Park, CA, is also developing a proprietary direct methanol fuel cell for application in consumer electronics. They have demonstrated an on-board battery replacement for a mobile phone that offers two to three times the energy density of standard lithium ion batteries. Polyfuel has funding from Intel, Mayfield, Ventures West, Technology Partners, and Chrysalix Energy Limited Partnership.

Smart Fuel Cell, based in Germany and founded in 2000, develops direct methanol fuel cells for portable power supplies, with one product on the market already. Based on specifications from its website, system energy density of prototypes for various applications is about 43 Wh/kg, while its standalone power supply (A25) is about 172 Wh/kg. Its new Energy Docking Station, jointly developed with Medion, allows users to power notebook computers when necessary, and operate by conventional battery or wall charger if desired, and will be displayed at the 2003 CeBIT show in Hanover.

In addition to those mentioned, there are many other small companies and efforts to produce micro fuel cells for portable electronics. The majority of these are based on direct
methanol fuel cells. More information can be found in the various marketing reports that have been published in the field by Frost & Sullivan, Allied Business Intelligence, and Fuji-Keizai.
4. Commercial Outlook

With evaluation of technology, intellectual property, and competitive products, a rough evaluation of the commercial outlook for micro solid oxide fuel cells can be made. Technologically, micro-SOFC potential is not yet fully realized due to challenges in thermal management, fabrication, and integration.

For application towards portable electronic devices, the issue of thermal management is critical. SOFC operating temperatures of 600°C or more can be brought down using thin-films technology and more conductive materials for the electrolyte, anode, and cathode. Thermal insulation for the stack becomes less difficult as the operating temperature drops, and stack heat loss can be minimized by correct packaging. Heat dissipation is important as well. Waste heat generated by the fuel cell must be either vented or absorbed. Fabrication challenges include creation of appropriate microstructures to maximize conductivity, component lifetime, and stack power density. Finally, integration of air/fuel delivery and exhaust gas systems must be resolved.

Another important issue is the cost of the system. Cost models have been developed for large traditionally fabricated systems, and could be used to estimate the cost of a micro scaled system. Lithium ion battery technology costs vary, one reports it to be about $0.77 per watt-hour [45], while another source reports $0.02 per watt-hour averaged over the lifetime of the battery [46]. Table 4-1 shows a short survey of available lithium ion batteries and cost per unit capacity.

<table>
<thead>
<tr>
<th>Type</th>
<th>mA-hr</th>
<th>Volts</th>
<th>W-hr</th>
<th>Price</th>
<th>Volume (cc)</th>
<th>Wh/L</th>
<th>Price per Wh</th>
</tr>
</thead>
<tbody>
<tr>
<td>LG-TM510 phone</td>
<td>900</td>
<td>3.6</td>
<td>3.24</td>
<td>$26.95</td>
<td>26.8</td>
<td>121</td>
<td>$8.32</td>
</tr>
<tr>
<td>Sony Ericsson T68i phone</td>
<td>700</td>
<td>3.6</td>
<td>2.52</td>
<td>$35.95</td>
<td>20.6</td>
<td>122</td>
<td>$14.27</td>
</tr>
<tr>
<td>Sony PCGA-BP4R laptop</td>
<td>5400</td>
<td>14.8</td>
<td>79.92</td>
<td>$499.99</td>
<td>670.6</td>
<td>119</td>
<td>$6.26</td>
</tr>
<tr>
<td>Sony Vaio GX700 laptop</td>
<td>4000</td>
<td>14.8</td>
<td>59.20</td>
<td>$209.95</td>
<td>235.9</td>
<td>251</td>
<td>$3.55</td>
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<tr>
<td>Compaq Presario 1830 laptop</td>
<td>3600</td>
<td>14.4</td>
<td>51.84</td>
<td>$130.95</td>
<td>214.6</td>
<td>242</td>
<td>$2.53</td>
</tr>
</tbody>
</table>

Table 4-1: Some typical lithium ion batteries for consumer electronics [19] [47].
If cost per total watt-hours is extrapolated from the data, assuming a 500 cycle lifetime for the battery, the mobile phone batteries range from 1.7 cents to 2.9 cents per watt-hour over the lifetime of the battery, while the initially more expensive laptop batteries range from 0.5 to 1.3 cents per watt-hour due to their higher energy capacity. Using this as a baseline, a rough estimate for the cost per watt-hour for fuel cells can be evaluated.

4.1 Micro Solid Oxide Fuel Cell Cost Approximation

The initial cost of the fuel cell can be estimated on a per watt basis. During use, the cost of the fuel can be added on a per watt-hour basis. The per watt cost will include the production costs. Thus an overall cost for the power can be calculated given the expected lifetime of the system. The cost per watt for a portable fuel cell has been estimated by one source to be $3 per watt [46]. A very rough approximation of cost to compare with can be calculated as well. These figures are used for illustration only, and while the data is accurate, the costs calculated are reasonable only within an order of magnitude.

Silicon wafer prices are typically quoted per square inch, and Dataquest report (Mar. 2000) quotes prices for various types of electronics grade silicon wafers as ranging from $18-$40 per square inch [48]. Use of non-electronics grade silicon wafers can be up to an order of magnitude cheaper. Assuming a 500mW/cm² power density in the fuel cell, a 2 cm² active area is required to produce 1W of power. Our previous assumptions on the active area to inactive area on the substrate can be used to calculate percent active area, which, for a 500x500 micron active cell on 600x600 micron substrate area, is 69.4%. This corresponds to a cost for substrates ranging from $8.04 to $17.87 per watt. A quick calculation of stack materials cost for the appropriate sized stack yields an additional 0.35 cents, due to the assumption of 500 nanometer thicknesses for stack components, which is negligible when compared to the cost for the substrate. Materials costs are assumed to dominate the overall cost of a solid oxide fuel cell fabricated by traditional means (tape casting), while equipment and labor costs combined represent the remaining 50% of the overall cost. Thus the stack cost per watt can be estimated to be approximately $16.09-$35.75 using standard silicon, but cheap silicon could reduce this to $1.61-$3.58 per watt. Additional components such as packaging and power conditioning for steady voltage output (necessary for function as a battery replacement) can double the cost. The rough final cost is then $3-$7 per watt generated.
In a separate cost model completed at Worcester Polytechnic Institute [60], cost per watt is estimated at $5.04. This cost model assumes a continuous processing model and places the bulk of the production cost in equipment and labor. Using 500 nm thick layers, powder materials to form targets, and a separate chamber for each sputtered layer, the total fixed cost for a 1,000,000 cell production capacity is $2.20 per cell, or $4.40 per watt. The remaining variable cost is primarily due to labor at $0.12 per fuel cell, with materials and energy expected to represent only $0.01 per fuel cell. Factoring in additional components brings the final cost per watt to about $10.

Operating lifetime can be estimated as a range from 2,000 hrs to 10,000 hrs of "operating time". Thus device use for eight hours a day will yield an overall lifetime of 250 days for a 2,000 hr fuel cell, and 3.4 years for a 10,000 hr fuel cell. Factoring the initial cost per watt into the lifetime, the cost per watt-hour is then calculated to be between 0.15 cents to 0.35 cents for a 2,000 hr fuel cell, and 0.03 cents to 0.07 cents for a 10,000 hr fuel cell. Using WPI’s model, the cost per watt-hour rises to 0.50 cents for a 2,000 hr fuel cell and 0.10 cents for a 10,000 hr fuel cell.

The fuel itself also has a cost. Butane as a commodity is about $0.26 per liter [49]. The retail cost of a butane refill for various applications ranges from about $30-$50 per liter, which reflects the additional cost of packaging and overhead costs. It is generally understood that higher purity fuel will be required for fuel cells to prevent degradation of the catalyst over time, perhaps resulting in a doubling of cost. Each liter of butane fuel carries 7700 watt-hours of energy, as previously stated. Assuming a system efficiency of 30%, the fuel cost per watt hour is then about 2.6 to 4.4 cents, averaging 3.5 cents. This is already much higher than the cost per watt hour for lithium ion batteries. As efficiency increases, the cost per watt-hour will drop proportionally. Total cost per watt hour for a 2,000 hr fuel cell is then between 3.4 cents to 6.2 cents per watt hour. If operating lifetime can be boosted to 10,000 hrs, cost drops to between 2.8 cents to 4.8 cents per watt-hour. The average of the max and min values are shown in table 4.1-1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Average cost of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium ion laptop batteries</td>
<td>0.9 cents/watt-hour</td>
</tr>
<tr>
<td>Lithium ion phone batteries</td>
<td>2.3 cents/watt-hour</td>
</tr>
<tr>
<td>2,000 hr fuel cell</td>
<td>3.8 cents/watt-hour</td>
</tr>
<tr>
<td>10,000 hr fuel cell</td>
<td>3.6 cents/watt-hour</td>
</tr>
</tbody>
</table>

Table 4.1-1 : Rough cost of operation for lithium ion batteries and micro-SOFC's.
From this rough calculation, the fuel cell costs about one and a half to four times as much as a battery to operate. The majority of the cost of operation stems from the fuel cost, which accounts for about 70% of the operational cost in the 2,000 hr fuel cell, and about 90% of the cost in the 10,000 hr fuel cell. Fuel costs are clearly important to the overall cost of operation, but initial cost may be the driver in the consumer marketplace. Clearly lithium ion batteries are much cheaper to operate in the long run with respect to total cost per unit energy, but micro solid oxide fuel cells can offer a higher energy capacity with no increased size or weight. It is also clear that the final consumer price of a first generation micro solid oxide fuel cell will be higher than the more mature lithium ion battery technology. What is not clear is whether the silicon infrastructure will drive manufacturing costs of micro SOFC’s down to the point where they are comparable with lithium ion battery technology.

4.2 Commercial Potential

The commercial potential of micro solid oxide fuel cells can be gauged by looking at the existing market for rechargeable batteries. This market is projected to be about $5 billion this year as shown in a recent report from IIT (figure 4.2-1), following a downturn in market size in ’01-’02.
Lithium ion batteries comprise the largest share of the market, followed by nickel-cadmium, nickel metal hydride, and finally lithium ion polymer. The largest applications for lithium ion and nickel metal hydride batteries are mobile phones and laptops as they are the most ubiquitous applications, while portable power for tools is largely handled by the NiCd battery.

Driven by the need for higher energy density and longer operating times, the portable power market will continue to expand. Micro solid oxide fuel cells are positioned to capture much of this market if the technical challenges are successfully and economically overcome. The inherently high energy density of hydrocarbon fuels, combined with robust operation independent of ambient conditions make micro SOFC's a strong competitor. Thermal management remains a key technological challenge, and development of an economic fueling solution will help drive widespread consumer acceptance. While polymer based micro fuel cells are slated for introduction in the next two years, micro solid oxide fuel cells are further from the consumer market, perhaps four to seven years away.

While growth is projected at a rate of 12%-17% [45], introduction of micro fuel cells could enable even higher growth rates. Since most portable electronics devices today are designed around battery lifetime, introduction of much higher energy dense devices may prompt introduction of a new breed of mobile electronics. This will undoubtedly replace many of the devices on the market today, in addition to creating a new high-end class of appliances for the mobile user. The enabling aspect of mobile power will drive the development of increased mobile functionality, perhaps creating a compelling technology that could rival the cellphone's tremendous growth in popularity in the late 90's. Market growth could be much larger than that predicted.

Current areas that will benefit greatly from micro SOFC technology include military and niche applications. Energy requirements for reconnaissance missions to power sophisticated military technology surpass today's best battery technology and will clearly increase in the future. The necessity for a more energy dense technology is strong. Today's micro fuel cell research programs and companies, while addressing these needs, will not only further the technology but also bring it closer to the consumer marketplace.
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