Design considerations for miniaturized PEM fuel cells

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Abstract

In this paper, we consider the design of a miniaturized proton-exchange membrane (PEM) fuel cell for powering 0.5–20 W portable telecommunication and computing devices. Our design is implemented on a silicon substrate to take advantage of advanced silicon processing technology in order to minimize production costs. The reduced length scales afforded by silicon processing allow us to consider designs that would be prohibited by excessive Ohmic losses in larger systems. We employ a mathematical model to quantify the effects of the secondary current distribution on two competing cell designs. In addition to the design of the cell itself, we discuss key integration issues and engineering trade-offs relevant to all miniaturized fuel cell systems: air movement, fuel delivery and water balance, thermal management and load handling. © 2002 Published by Elsevier Science B.V.

Keywords: PEM fuel cells; Silicon processing technology; Silicon-based microreactors; Miniaturized fuel cell

1. Introduction

Consumers, now, have available to them a wide array of portable electronic telecommunication and computing devices, including cellular telephones, personal digital assistants, portable computers, game devices and music systems. It is expected that these machines will become more numerous and more diverse in the coming years. Wireless digital communication and advanced computing technologies are merging to combine computing and communication functions, essentially packing more functionality into ever-decreasing volumes. While the trend is that electronic components are becoming more efficient and each component demands less power with each generation, the ever-increasing functionality of these devices means that each device includes more components thus increasing the overall power required. The demand is for energy storage devices that will allow these devices to operate for longer times without being plugged into an electrical outlet.

While battery technology has improved considerably in recent years, the functionality, operating speed and lifetime of many portable devices are still limited in how long they can operate as truly portable (i.e. unplugged) devices by the quantity of energy that can be stored within them. Fuel cells, however, provide significant advantages over conventional battery systems. A direct methanol proton-exchange membrane (PEM) fuel cell combined with a container of methanol promises approximately a 10× improvement in energy density. Similarly, with sufficient advances in hydrogen storage density a hydrogen-based fuel cell and hydrogen storage system may provide a significant increase as well. (Preliminary investigations indicate that increased hydrogen storage densities might be achieved in carbon fibers or lightweight metal hydrides.) Furthermore, rather than relying on slow, reversible recharging as in secondary batteries, a fuel cell offers the possibility of rapid, nearly instantaneous recharging by simply adding more fuel to the reservoir in the device.

Presently, most fuel cell research targets stationary premium power and automotive applications and stacks capable of delivering approximately 1–200 kW. The large cells are typically mechanically compressed sandwiches of graphite composite electrodes and membrane assemblies. To create a miniature fuel cell for portable devices that delivers power in the range of 0.5–20 W, one will not achieve an optimum design by simply scaling down the larger system. Rather, one must redesign each component of the fuel cell with an eye towards miniaturization. We seek to miniaturize the fuel cell by following the example of silicon-based microreactors. Power conditioning can be incorporated into silicon, along with process and control circuits. An extrapolation of this trend leads one to consider the incorporation of power

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generation at the chip level. Fuel cells based upon a silicon substrate will not match the raw materials costs of traditional (carbon-based) fuel cell components, but if packaging, integration and on-chip control become cost drivers for the system, the silicon-based fuel cell power source will offer advantages over the more traditional carbon-based embodiments. Therefore, we present a design for a miniaturized PEM fuel cell to power portable electronic devices. The improved energy density is expected to improve the functionality of such devices and enable their sustained operation remote from the power grid.

Our work on the miniaturized fuel cell draws inspiration from the work of Prof. Klavs Jensen and his research group at the Massachusetts Institute of Technology. His group has pioneered the development of microreactor systems, including a partial oxidation reactor [1]. A primary advantage of the silicon-based approach is the ability to control thin-film properties and their interfaces, enabling one to optimize reactor performance. Additionally, one can leverage decades of knowledge and the facilities developed for processing integrated circuits and micro-electromechanical (MEMS) devices. Process sensors and control logic can also be built into the same substrate, facilitating on-board closed-loop control.

Our initial prototypes of a miniaturized fuel cell directly adapted the designs of conventional fuel cells using silicon as a support structure in lieu of graphite current collectors; this design is shown in Fig. 1. Nafion membranes were painted with electrode catalyst inks as per the work of Wilson and Gottsfield [2] and introduced into a sandwich structure. Initial tests (Fig. 2) demonstrated materials
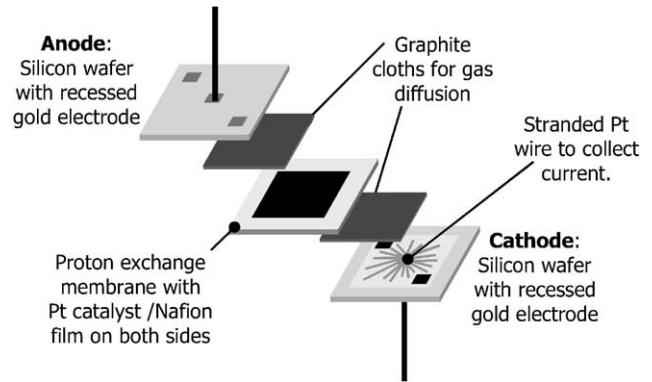

Fig. 1. Schematic diagram of first silicon-based hydrogen/oxygen fuel cell prototype.

compatibility and indicated that the system was limited by Ohmic losses and interfacial contact resistance. Our continued efforts focus on attempts to reduce these Ohmic losses and integration of more Si processing steps into the construction process, thereby reducing the number of elements that must be put together by hand.

2. Our approach: bilayer and monolithic designs

We present a design for a miniaturized fuel cell integrated into a silicon substrate. We evaluate two alternative designs—a bilayer design using separate Si wafers for the anode and cathode that are subsequently sandwiched together and a monolithic design that integrates the anode and cathode onto a single Si surface.
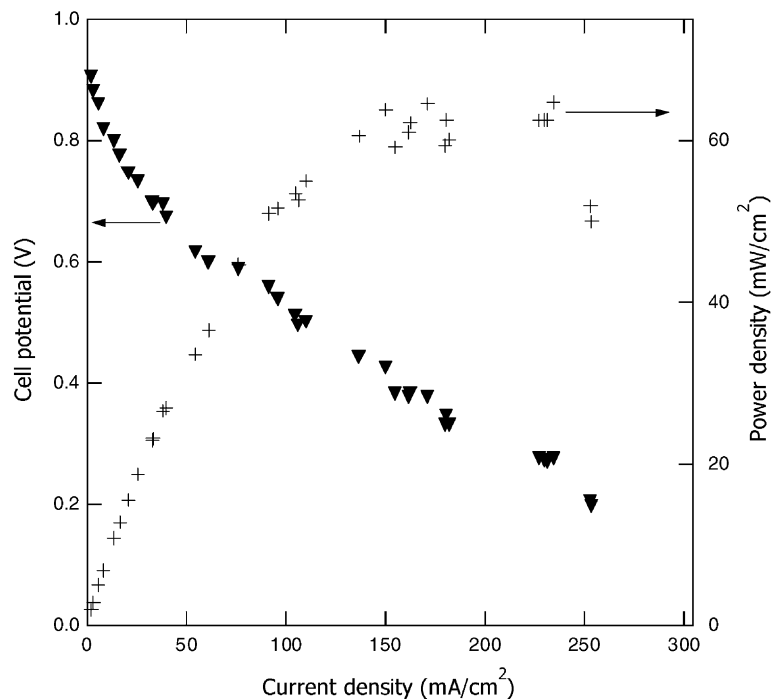

Fig. 2. Performance curve for initial prototype, operating on hydrogen/oxygen 1 atm, high stoichiometric flowrate at room temperature.
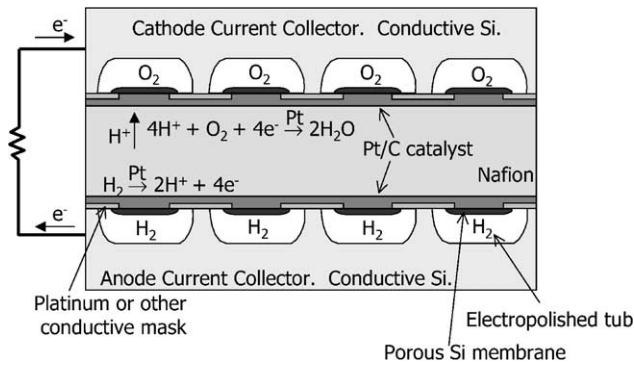
Fig. 3. Schematic diagram of bilayer design.

Fig. 4. Electropolished tunnels beneath porous silicon layer prepared by electrochemical etch. Photo from [3].

The bilayer design is depicted in Fig. 3. This design is similar to the standard cell sandwich commonly used in PEM fuel cell systems, albeit with different materials and means of construction. In our design, the anode and cathode are constructed from conductive silicon wafers. The reactants will be distributed around the face of the silicon wafer through a series of tunnels. The tunnels are created by first forming a porous Si layer and then electropolishing away the Si from beneath the porous film. This process was developed at the MESA Institute at the University of Twente [3] and a photo from their results is shown in Fig. 4. Once the tunnel structures are complete, we complete the formation of the fuel cell by adding a catalyst film on top of the tunnels and finally, by casting a proton-conducting membrane, e.g. Nafion[2] from solution. Two of these membrane-electrode structures (one for the anode, another for the cathode) will be made and then sandwiched together. The ability to control the thin-film properties and their interfaces will facilitate optimization of the device performance. For example, it is expected that exploiting the chemical adhesion of layers can improve device reliability over reliance on mechanical compression or thermal treatments.

We form silicon tunnels by controlling the process conditions in an electrochemical etching process. The rate-determining step for the electrochemical dissolution of Si is the concentration of either of holes or of fluorine-containing ions at the active surface [4]. If it is the latter, then trench features will etch more quickly at the top of the feature than at the bottom, tending to create a smooth surface (i.e. to polish). If the concentration of fluorine-containing ions at the surface is sufficient, then the reaction will be limited by the concentration of holes. In this case, as an initially smooth surface begins to etch, statistical fluctuations will cause peaks and valleys in the surface. In p-type semiconductors, the formation of a geometric peak increases the local electric field, forcing holes out of that region. The local etching rate decreases until all holes are forced out, the etching ceases and the residual material is no longer conductive. It is this action that forms the network of pores that is porous Si. Therefore, whether one forms porous Si or electropolishes
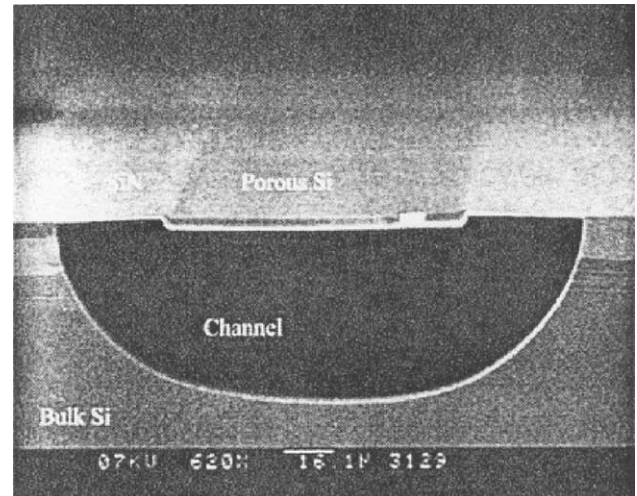
depends upon the processing conditions: the HF concentration of the etching solution, the current density and the dopant type and dopant concentration.

One can, therefore, start with a silicon wafer and form a porous Si layer on the surface, transforming the conductive Si into an insulator. By then changing the processing conditions to move into an electropolishing regime, the insulating porous film is left intact and the polishing begins beneath it. If the substrate is initially patterned such that the porous layer is supported on either side, then you are left with a porous Si layer suspended above a void. Note that both reactions (forming porous Si and electropolishing) proceed isotropically, affecting the resulting tunnel shape.

We are also considering a monolithic design, shown in Fig. 5, in addition to the bilayer design presented in Fig. 3. The monolithic design is essentially an "unfolded" fuel cell with the anode and cathode on the same substrate. It is important to note that while this monolithic design shares a planar side-by-side electrode configuration with the "strip cell" design, it is not the same as the design proposed in either Dyer's work [5] or the design of Calabrese Barton et al. [6]. In these two designs, fuel and oxidant are mixed together in the same flow channel; a cell potential is generated by the selectivity of each electrode for either the anodic or cathodic reaction.[3] In our monolithic design, fuel and oxidant are delivered to the cell in isolated, separate (but adjacent)

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[2] Nafion is a registered trademark of E.I. DuPont de Nemours.

[3] In the work of Calabrese Barton et al., care is taken to ensure that each electrode is inactive for the undesired (competing) reaction. In their design, the methanol electrode is covered by a Nafion film (largely impermeable to oxygen); the cathode uses an electrode that will not catalytically activate the methanol oxidation reaction. Dyer's approach requires that the component in the fuel/oxidant mixture that is more active, be consumed on the near side of a separator; the reactant that is consumed to a lesser degree is then free to diffuse across a separator to the opposite electrode. Both designs put out low power: Calabrese Barton's methanol fuel cell due to the relatively poor kinetic performance of the selective oxygen catalyst and Dyer's due to the limitations of running a cell with a mixed potential.
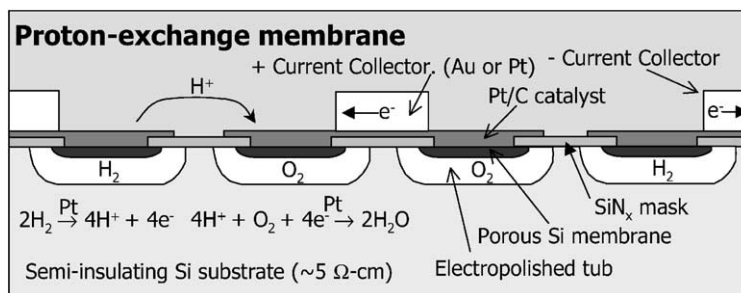
Fig. 5. Schematic diagram of monolithic design.

channels. The isolation of fuel and oxidant will ensure safety and reduce susceptibility to cell reversal with gradual poisoning of the electrodes.

A primary advantage of the monolithic structure is the ability to form all of the components on the same structure, analogous to IC or MEMS manufacturing. Additionally, since the top surface is now the moisture-sensitive membrane, this design enables the humidification control of the membrane to be separated from other control circuits, e.g. reactant flow and temperature stability. It is also worth noting that, with this design, one can achieve very small separations between anode and cathode without the difficulty in casting very thin pinhole-free films. The membrane can be made as thick as is dictated by casting limitations, while still keeping anode and cathode close together, simply by how they are arranged on the substrate. One can also size the two electrodes differently, enhancing the surface area of the more sluggish electrode to improve its performance. One must have the same total current at each electrode. Because the kinetic losses are a function of current density, however, one can increase the surface area of the slower electrode, thereby attaining the same total current for a lower current density and, hence, lowering kinetic losses for that electrode.

On the down side, however, "unfolding" the fuel cell structure reduces the power density on a substrate area basis by 50%, since the anode and cathode now share a single substrate. The other difficulty with this structure is that the current must now be pulled out by the metal lines, requiring them to be relatively large. In the bilayer design, the entire Si substrate is used as a current collector.

3. Comparison of bilayer and monolithic designs

In addition to the fact that the anode and cathode must share silicon real estate silicon substrate in the monolithic design, the coplanar arrangement induces a non-uniform current distribution on the surface of each electrode. This distribution is due to the fact that some portions of the electrode are more accessible for current than others. That is, the protons generated at the anode have a shorter path (and hence, less Ohmic drop) to reach the near part of the cathode, than the portion of the cathode located further away from the

anode. The Ohmic drop tends to enhance the local current density at the near region of the cathode and suppress it at the remote part. We have developed a simple mathematical model to examine the effects of the cell design on performance. By running a series of simulations, we can determine quantitatively how the bilayer design compares to the monolithic design.

We employ a simple model to determine the secondary current distribution in the monolithic design. The model considers only kinetic losses at the cathode and Ohmic losses in the membrane separator. We do not consider the limitations of mass-transport of reactants (fuel or oxidant) to the electrodes. Furthermore, we assume that the water content is uniform throughout the thickness of the membrane separator; correspondingly, we neglect spatial variations in the ionic conductivity. It is assumed that the bilayer design affords a uniform current density across the surface of both electrodes; the model for the bilayer design reduces to a simple linear Ohmic drop across the membrane and Tafel kinetics at the cathode. We neglect kinetic losses at the anode.[4]

The current density at the cathode is related to the local surface overpotential by Tafel reaction kinetics (here we employ the convention that at an interface, the current is positive if it is an anodic current and negative if it is a cathodic current):

$$i = -i_0 aT \, \exp\left[-\frac{2.303}{b}(\Phi_1 - \Phi_2 - U)\right] \tag{1}$$

where i_0 is the exchange current density (A/cm^2) of the catalyst surface (a kinetic parameter), a the specific surface area of the electrode and T is the thickness of the catalyst layer. It is important to distinguish between T, the thickness of the catalyst layer and L_{cath}, the width of the catalyst layer. The width of the catalyst layer is used later to denote the smaller dimension of the cathode in the plane of the substrate; the thickness, T, is the dimension normal to the substrate surface. In our model, we lump the terms $i_0 aT$

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[4] The neglect of anode kinetic losses is acceptable for a PEM fuel cell operating on hydrogen as a fuel, but this simplification will not accurately predict the performance of a methanol fuel cell, as kinetic losses for methanol oxidation are a significant restriction on cell performance.

Table 1
Parameters in kinetic expression for cathode

$i_0 aT$ (μA/cm^2)	17.1
b (mV per decade)	134
U (V)	1.229

Table 2
Parameters for base case in monolithic design simulations

Separation distance (μm)	50
Anode width (μm)	25
Anode current collector (μm)	2
Cathode width (μm)	25
Cathode current collector (μm)	2
Membrane thickness (μm)	50
Conductivity (S/cm)	0.1
Separation distance (μm)	50

These values are used in all simulations unless otherwise indicated.

into a single lump term to describe the kinetics of the reaction (each individual term in this lump term is not determined separately). The numerical values are determined from fitting experimental data on a cell operating on hydrogen for a stable catalyst layer as constructed by the group at Los Alamos National Laboratory [7]. The term b in the exponential is the Tafel slope and the numeric constant 2.303 is the natural logarithm of 10, necessary for converting from the exponential to base 10. U is the equilibrium potential for the oxygen reaction relative to a reversible hydrogen electrode. Φ_1 is the potential of the positive electrode; Φ_2 is the potential of a point in the membrane adjacent to the electrode, measured by a hypothetical reversible hydrogen electrode. Values used in the kinetic expression are shown in Table 1.

In order to explore the effects of the monolithic design, we reduce the problem to a secondary current distribution on the cathode. As in the description of the bilayer design, the kinetic losses at the anode are neglected. It is assumed that the entire anode surface sits at a constant potential equal to that of a reversible hydrogen electrode. (This condition is maintained if the reaction kinetics at the anode are very fast; if the anode potential deviates from the reversible potential, then the current at that electrode would be tremendously high. For current densities within our range of operation, then, deviations from the reversible potential at the anode are neglected.) The current density in the membrane is described by Ohm's law:

$$i = -\kappa \nabla \Phi \qquad (2)$$

where κ is the ionic conductivity of the membrane. Assuming uniform conductivity, the conservation of current in the membrane reduces the equation to Laplace's equation for the potential:

$$\nabla^2 \Phi = 0 \qquad (3)$$

There are three different boundary conditions for Eq. (3), depending upon the local surface:

$\Phi = 0$, at the anode;

$\dfrac{\partial \Phi}{\partial n} = 0$, at insulating surfaces and planes of symmetry;

$-\kappa \dfrac{\partial \Phi}{\partial n} = f(\Phi)$, at the cathode $\qquad (4)$

The current density is determined by the local potential gradient. At the cathode, conservation of current requires that the current flowing in the membrane adjacent to the cathode be set equal to the interfacial current, specified by Eq. (1).

The current distribution is solved by means of the Schwarz–Christoffel transformation [8], which maps points that lie on the perimeter of a polygon on to a single line. The points on this line are then mapped onto yet another polygon, where the two electrodes are now opposite faces of a rectangle. This transformation is shown in Fig. 6.

Because Laplace's equation in the actual geometry (Eq. (3)) reduces to Laplace's equation in the transformed geometry, the solution with boundary conditions specified by Eq. (4) reduces to a simple series of cosines and hyperbolic sines:

$$\Phi = a_0 v + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi v}{v_{\max}}\right) \sinh\left(\frac{n\pi u}{v_{\max}}\right) \qquad (5)$$

The form of the solution satisfies the boundary conditions at the anode and on the insulating surfaces. The anode lies on the line where $u = 0$, and because $\sinh(0) = 0$, the form meets the condition for the anode potential. Similarly, the insulating surfaces lie at the positions $v = 0$ and $v = v_{\max}$ and the condition that the normal gradients at these points be zero is met by the condition on the cosine term. The only complexity now lies in the fact that there is a scaling factor in transforming the normal potential gradient in the real geometry to the normal potential gradient in the transformed geometry. Because the transformation is not a linear transformation, the scaling factor varies as a function of position. We solve for the appropriate terms in the series solution (Eq. (5)) by truncating the series at 40 terms and then applying the cathode boundary condition at 40 evenly-spaced mesh points on the cathode grid.[5] The relevant length scales and the ionic conductivity of the membrane used as the base case in the simulations are listed in Table 2.

The initial results are shown in Fig. 7. This shows the potential as a function of current density for both the bilayer design and the monolithic design for a series of electrode lengths in the monolithic design. Current densities in this configuration are based upon the surface area of the cathode alone. This graph demonstrates that for larger feature sizes, the monolithic design utilizes the cathode area less

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[5] The number of mesh points was set to 40 after a demonstration, that this number is sufficiently large, that there was no discernable difference between running the simulation with this number of mesh points and a significantly larger number.
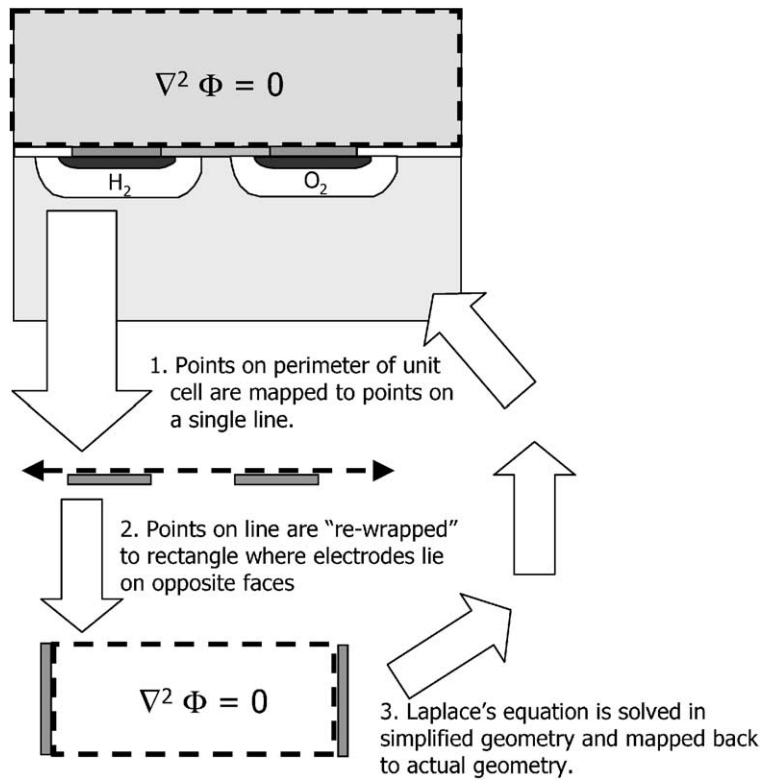
Fig. 6. Illustration of solution strategy for current distribution using Schwarz–Christoffel transformation.

effectively because only the region of the electrode nearest the anode gets utilized. For smaller feature sizes, however, the monolithic design actually matches and can even exceed the bilayer design for the same separator distance. This is
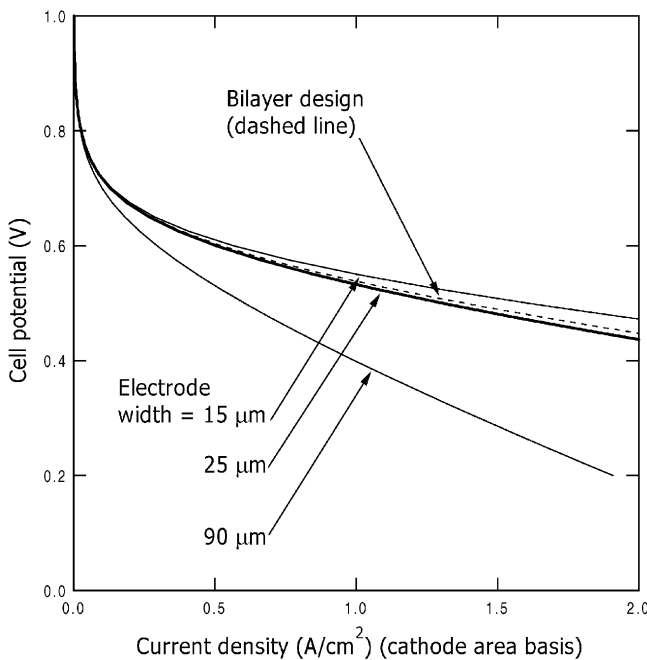

Fig. 7. Comparison of current densities for bilayer and monolithic designs. Current densities are expressed on the basis of cathode surface area, not total cell surface area.

due to the fact that current can flow throughout the entire volume of the membrane and for sufficiently small electrode widths, there is not too much of an Ohmic penalty paid for current to reach the center or far region of the electrode.

Fig. 7 presents results based upon cathode surface area, a valid concern primarily when the predominant cost of materials is the catalyst within that layer. In that case, one would want to maximize the current per unit catalyst and the total amount of catalyst will scale with the area of that electrode. If, however, one is really concerned with the optimization of power density on the basis of total area of the cell, one must consider a different figure. Fig. 8 shows the results of current density on a total substrate area basis and here the bilayer design is superior for all configurations. Even when dividing the current density of the bilayer design by 2 (dashed line in Fig. 8) to reflect the fact that one needs two silicon surfaces to complete a bilayer cell, the performance exceeds that of the monolithic design. This is due to the fact that the monolithic cell must also devote some of its surface area to the separator and the current collectors, in addition to dividing area between the anode and cathode.

If one considers overall cell volume, instead of simply considering cell area, however, the monolithic design still lags the performance of the bilayer design, though not by as much as is indicated by the performance on a per total area basis. Fig. 9 shows the current density generated per unit volume of cell area, defined as the thickness of the membrane and the silicon substrate. It is the product of projected area (the same basis as in Fig. 8), multiplied by the thickness
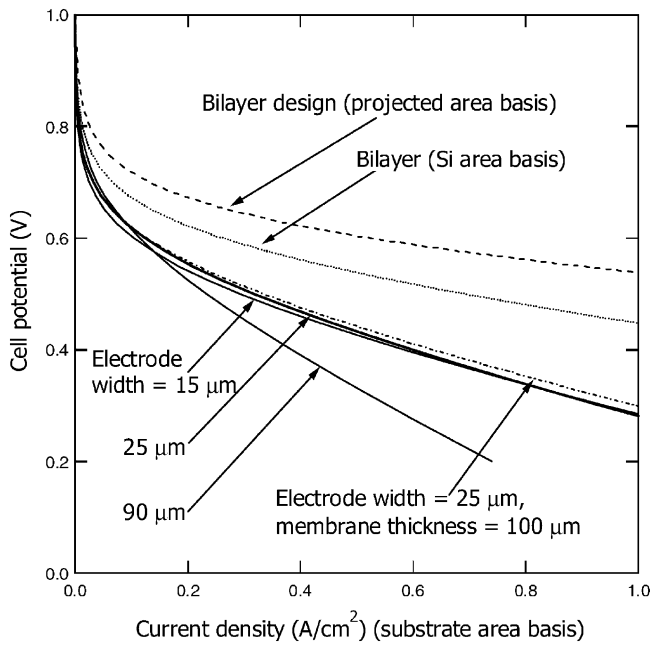
Fig. 8. Comparison of current densities for bilayer and monolithic designs. Current densities are expressed on the basis of substrate area. For monolithic design, membrane thickness is 50 μm unless otherwise specified. The thicker membrane affords greater current per unit area, because the Ohmic losses are lowered as the current is spread out over a larger volume within the membrane.
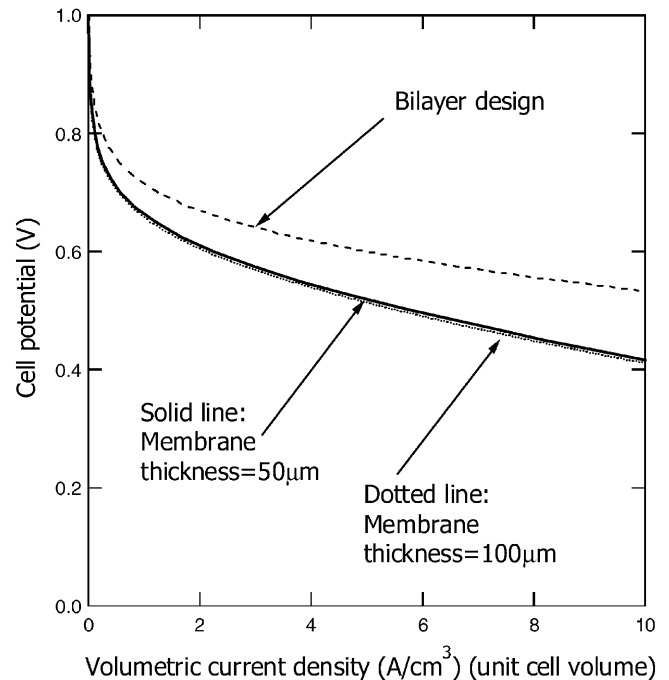

Fig. 9. Comparison of current densities for bilayer and monolithic designs, based upon volume of unit cell. All electrode and separation thicknesses are as in Table 2 unless otherwise noted.

of membrane plus substrate that determines this volume. The bilayer design is penalized on a volumetric basis because it requires two pieces of silicon to construct a single cell and the silicon wafers are larger than the thickness of the membrane. The silicon wafers are ∼500 μm thick, compared to a membrane thickness in the order of tens of microns. While, in theory, the silicon substrate could serve as a bipolar current collector with an anode on one side and a cathode on the other, in practice, this would be quite difficult to integrate into a process.

Fig. 9 presents the data in such a way that makes the monolithic design appear to lag the performance of the bilayer design only slightly (in terms of the penalty in cell potential at a given current density). This might be a trick of the way that the potential versus current density graph leads us to interpret data. If we see what the current density is for a given potential (rather than the other way around, as we tend to do on an *x*–*y* graph), the bilayer design more dramatically outperforms the monolithic design. Fig. 10 displays the power density as a function of current. When plotting the power density per unit cell volume that can be obtained with the two designs, we see the bilayer design remains the clear winner, with a peak power density more than double that of the monolithic design. While the performance of the monolithic design still lags the bilayer design, the simplicity of the single substrate construction might still lead one to adopt the monolithic design.

The simplicity of construction might lead one to adopt the monolithic design despite poorer volumetric power density,

but the one must consider the complexity of delivering reactants to the cell and the overall system construction. Fig. 11 shows a top–down comparison of the substrate for each design. While the extreme aspect ratio for each flow pass in the monolithic design is an exaggeration of what one would want to use in practice, it does illustrate an important point: that the flow channels lie in a single plane precludes one from crossing the fuel and oxidant streams. In addition, one must put down metal lines to pull the current, because
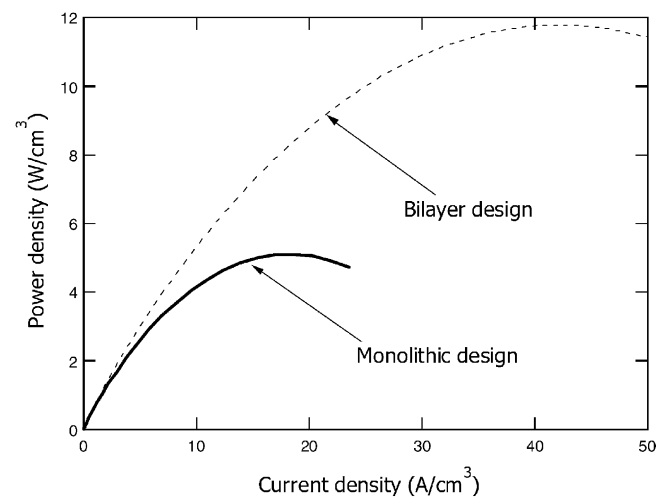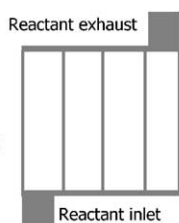

Fig. 10. Comparison of power densities for bilayer and monolithic designs, based upon volume of unit cell. All geometric parameters for monolithic design are as given in Table 2.

Bipolar design:
fairly simple-
electrical contact through back
gas flow channels in substrate

Reactant exhaust

Reactant inlet

Monolithic design:
connections are much more complicated;
can not intersect flow channels on same level
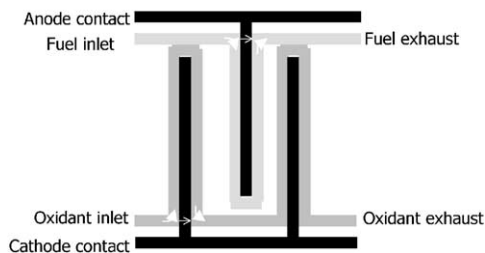separate electrical contacts (nonconductive Si)

Anode contact
Fuel inlet
Fuel exhaust
Oxidant inlet
Oxidant exhaust
Cathode contact

Fig. 11. Illustration of top–down design complexity of bilayer and monolithic designs.

the silicon substrate must be insulating, lest the electrodes short one another out. The bilayer design is simple compared to the more complicated series of structures in the monolithic design. The monolithic design, then, offers simplicity only in the stepwise integration of substrate, electrodes and membranes. This simplicity is paid for, however, both in power density and in terms of complexity within the substrate.

4. System considerations

A fuel cell delivers high-power per unit mass and if it uses liquid or solid fuels, it offers high levels of power and energy per unit volume as well. The problem with using a fuel cell stack for portable (or even automotive) power delivery, is that the stack must be incorporated in a complete system that meets all the power demands of the device that uses it. The best performance from a fuel cell is obtained when hydrogen and oxygen are continuously supplied to the fuel cell stack and the stack simply converts the chemical energy to electrical energy at an unregulated voltage. A portable power system, however, must deliver a reliable, well-regulated voltage and be able to respond to changes in power demand rapidly. Therefore, a fuel cell stack is not the only component in a portable power system. If one is trying to design a fuel cell based power system that can be used in portable electronic devices without radically altering the form factor of the device, one must consider the design of the entire system, not just the cell stack itself. The system must be designed to provide the necessary reactants to the fuel cell, remove the by-products and to regulate the system, all

while minimizing volume, mass and if at all possible, system complexity.

There are certainly a diverging number of paths that might be taken to deliver a portable fuel cell device. It is far from decided whether hydrogen or methanol will be the fuel of choice in the first power systems to reach the market. A wide variety of cell designs have been proposed, each with its own merits and limitations. In designing a complete power system, there are several issues that must be addressed, regardless of the design of the fuel cell itself. Here, we discuss what are some of these technical challenges and their importance.

5. Air movement

While much attention has deservedly been focused on the selection of fuels for the fuel cell, the transport of oxidant to the cathode is another very important issue for portable fuel cells. Based upon volume and weight constraints, it is advantageous to use oxygen from air to serve as oxidant for the fuel cell. Using air means that only the fuel must be stored with the device.

The consumption of oxygen by the fuel cell, however, ensures that the local oxygen concentration adjacent to the cathode will be depleted as current is passed. In a completely passive system (i.e. one without any active means of air movement) the entire surface area of the fuel cell cathode must be exposed to the exterior of the device to allow oxygen to reach the catalyst layer. The amount of oxygen that can reach an exposed electrode will start out to be much greater than the maximum oxygen demand of the electrode, if the device is powered for only short duty cycles, oxygen diffusion should not be a limitation. For longer discharges, however, in the absence of convection, the local oxygen concentration will deplete and the path length for oxygen diffusion will increase. Eventually, passive air breathing for a planar configuration will be insufficient to meet the oxygen demand of the fuel cell, unless one has a very large exposed surface area.

Oxygen transport limitations will be even more prominent for a fuel cell operating with liquid-feed (i.e. a direct methanol fuel cell) because the presence of liquid water at the anode will lead to higher water content at the cathode and will consequently restrict oxygen transport to the cathode surface. Even if one neglects the tendency of oxygen transport to decrease with time in a passive planar design, it can be shown that the absence of active air movement can lead to problems with integrating fuel cells into portable devices. Without active air movement, one must expose a majority of the cathode to its surroundings in order to allow air to access the electrode. This places a large demand on the external "real estate" of the portable electronic device.

Fig. 12 is a schematic depiction of the surface area required for a fuel cell operating at peak power to power
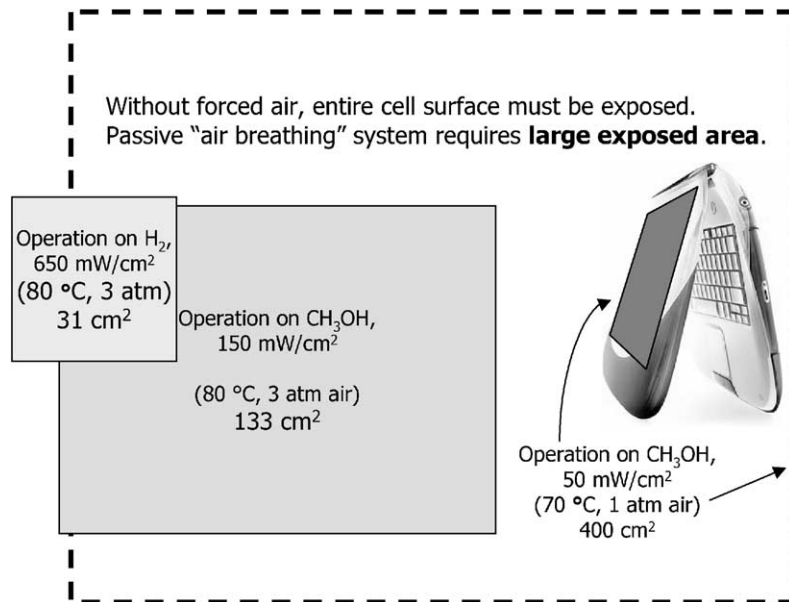
Fig. 12. Illustration of exposed area required to deliver oxygen demand for a fuel cell providing power to a 20 W laptop computer, in the absence of active air movement.

a 20 W laptop computer. The data for power density (W/cm^2) are taken from recent data from Los Alamos National Laboratory for cells operating on hydrogen and on methanol [7,9,10]. If one operates the cell on neat hydrogen, only approximately 31 cm^2 are required to ensure that the cell assembly can deliver the peak power of the device. The lower efficiency of methanol oxidation relative to hydrogen oxidation requires a greater surface area for the cell stack to meet power demands (roughly 133 cm^2 for cells operating at 4.8 bar air and 80 °C). If one assumes that the stack must operate at 70 °C and at atmospheric conditions, the required surface area increases to 400 cm^2, a significant portion of the total external surface area of a typical laptop computer.

There are ways to increase the surface-to-volume ratio in order to ensure that more of the fuel cell is exposed to air and the radial air breathing design [11] is one way to solve this problem, provided that one is prepared to locate the power system outside of the portable device itself. This design allows the fuel cell to operate passively, without any pumps or active movement. If, however, one wishes power a portable device without radically altering the form factor of the device itself, one must include a means of air movement to bring oxygen from outside the system to all of the cells in the stack.

6. Fuel delivery

A portable power system must contain both the fuel cell and the means of fuel storage and delivery. Unless one is willing to consider the inclusion of a reformer in the power system (which leads to some rather complicated thermal management due to the higher operating temperature of the reformer), one is left with two choices of fuels: hydrogen and methanol. Hydrogen as a gas requires a very large volume and therefore negates one of the key advantages of a fuel cell power system, namely, the increased power per unit volume. One can store hydrogen by means of metal hydrides or, possibly, carbon materials, but even with the best metal hydride storage densities, liquid methanol has roughly three times the energy per unit volume that metal hydride storage does. Carbon nanotubes have been studied for hydrogen storage [12] but there is great variation among reported values of energy density. It has not been suitably demonstrated that carbon nanotubes will store hydrogen sufficiently or reproducibly enough to use in an energy storage system.

If one wants to increase the amount of time elapsed between refueling a portable power system while keeping the size of the system to a minimum, then it is necessary to maximize the energy stored per unit volume of fuel. Therefore, at least with the current capabilities of hydrides and carbon storage, the fuel of choice should be methanol. The choice of methanol complicates the system, however. Because methanol kinetics are poorer than hydrogen oxidation, the size of the cell stack must be increased. The inefficiencies of the methanol oxidation process also result in greater losses and a greater heat load that must be managed by the system.

One would also like to operate on as pure a methanol solution as possible, because methanol carries the energetic content and diluting the methanol concentration reduces the energy per unit volume of the system. Operating with very rich methanol solutions at the anode (i.e. solutions where methanol is the majority component and water is a relatively

small fraction of the mixture) results in incomplete oxidation products such as formaldehyde [13]. These incomplete oxidation products are far less desirable than carbon dioxide as a reaction product. While it is possible to store methanol as the fuel and add it to a water stream just upstream of the fuel cell, this mixing process does add some complexity to the overall system.

One must also consider that, while hydrogen fuel cells can operate in the range of 60–100 °C, this temperature range requires careful consideration when operating with a methanol mixture as the fuel. The regular boiling point of methanol is 65 °C, so cells in excess of this temperature must be operated with a slight back pressure on the anode to prevent the feed stream from boiling.

Also, when operating with methanol as a fuel, one must address the problem of methanol crossover. Methanol crossover is the process by which methanol diffuses across the fuel cell from anode to cathode. Because the PEMs that electronically isolates the anode from the cathode is swollen by water (and indeed, it is water that allows PEMs to have such favorable ionic conductivities), the chemical similarity between methanol and water ensures that methanol can readily permeate the membrane as well. This results in a lower conversion efficiency, as some of the methanol is directly consumed at the cathode, resulting in a release of heat rather than being oxidized solely at the anode to produce electrical current. This phenomenon also means that control must be maintained to ensure that methanol does not continuously diffuse across the cell to burn away at the cathode when the cell is not providing power.

There are several approaches to mitigate methanol crossover. New membranes promise to tune the physical properties of the PEM to allow high ionic conductivities with drastically reduced methanol permeability, but with materials that are currently available to developers, two main approaches can be considered.

The first crossover mitigation scheme involves the regulation of the methanol feed concentration. The crossover rate is roughly proportional to the excess methanol concentration at the anode, i.e. the concentration in excess of the amount needed to ensure adequate methanol diffusion from the flow channels to the anode catalyst layer. By maintaining a feed concentration just above the minimum necessary to provide methanol to the anode, one can severely mitigate the crossover rate. This approach works quite well if one knows what the load profile will be in advance, but it does have drawbacks. If one has chosen the methanol feed concentration to deliver a concentration selected for low-power levels, it prevents one from instantaneously stepping up the power output of the device. This technique also requires more complicated feedback to monitor and adjust the methanol concentration at the inlet to the fuel cell.

The other technique is to insert a barrier layer within the fuel cell. The barrier is generally permeable to hydrogen (either as ions or as atomic hydrogen), but it rejects methanol. It effectively reduces methanol crossover, but it adds to the complexity of the unit cell and introduces at least one additional interface, with the added resistance such an interface implies. As a result, less power can be delivered per unit cross-sectional area [14].

A final concern with respect to fuel delivery is the problem of utilization. One wants to use as much of the fuel as possible. The problem, however, is that if nearly all of the fuel is used, the delivery of the fuel to the electrode becomes increasingly difficult. Diffusional mass-transport limitations restrict the rate at which the last bit of fuel can reach the electrode. If one is operating at high utilizations, there will be a significant drop-off in current density at the downstream (i.e. depleted) region of the flow channel. This means that one has to dedicate a significant portion of the fuel cell area to reacting the last bit of fuel. Indeed, once one has depleted the reactant sufficiently, the local current density will be proportional to concentration, or put another way, inversely proportional to the quantity $(1-u)$, where u is the fuel utilization. This means that to achieve complete utilization of the fuel, one would need an infinite area.

When operating on hydrogen, one can still get reasonable performance operating with a dead-end hydrogen flow [15] (implying very high hydrogen utilization), because of the rapid diffusion of hydrogen. When operating on methanol, however, one can not afford to run the cell to full utilization because of the precipitous drop in cell potential one must endure in doing so. Therefore, methanol must either be recycled or be expelled (unreacted) from the system. One is reluctant to expel methanol out of the system, however, as it is a toxic material. A recycle stream is a suitable way to lower the utilization without rejecting the fuel, but this presents greater complexity in the system.

If one simply wants to deliver fuel from a reservoir to the fuel cell in a single pass, it is relatively straightforward. One simply starts out the reservoir at a much higher pressure than the operating pressure of the fuel cell and this driving force will send fuel from the reservoir to the cell. All one needs to regulate the flow of fuel from the reservoir to the cell is a valve, which can be fairly easily included, although the energy required to open and close a valve must be considered, if it is used to regulate the flow of fuel dynamically. If one tries to integrate a recycle stream, however, one must now include a pump to raise the pressure from the downstream and this will definitely act as a parasitic load on the system. When operating on methanol with a recycle, one must also then include a scrubber to lower the carbon dioxide content of the recycled stream, lest it start to boil out of solution and occlude the flow channels.

7. Water balance

Another concern in the system is the issue of water management. While it is possible to operate a fuel cell passively without any active control over the water flow

in and out of the device, performance enhancements can be achieved if one is able to move the water within the device from where it is produced in excess to where it is often depleted.

In a hydrogen fuel cell, the concern is operation on a dry anode fuel stream. PEM require water to swell and have suitable ionic conductivity. In the absence of sufficient hydration, the membrane is too dry and the Ohmic drop across the membrane becomes large. At higher current densities, however, the water produced at the cathode can condense and form a thin liquid film that blocks oxygen transport to the cathode. Particularly in the case where there is no active air movement to enhance the removal of water, the water content at the cathode can build up until flooding occurs [16].

The conductivity of the membrane is not generally a problem for liquid-feed methanol fuel cells, because the liquid at the anode does a good job of swelling the membrane and ensuring low Ohmic drop across the membrane. There is a need to deliver water to the anode, however, water is a necessary reactant in the oxidation reaction. In the absence of sufficient water at the anode, the methanol will not be converted to carbon dioxide and the anode performance will drop considerably. The problem of flooding is often even greater in methanol fuel cells, where the liquid-feed raises the average water content of the membrane and induces the transition to condensation at the anode to lower current densities.

The hydrogen fuel cell needs water delivered to the anode to increase ionic conductivity; the methanol fuel cell needs water present at the anode to enhance electrode reactivity. Both systems have the same basic water management concerns, however. In both fuel cell systems, one must remove excess water from the cathode and deliver some of it to the anode while rejecting most of it to the environment. The degree to which these demands can be met within the constraints of the device, will have a significant effect on overall system performance.

8. Thermal management

Thermal management is an important consideration for portable power devices. Already, laptops and cellular phones are constrained by the ability to dissipate the heat generated during their use. Processor speeds in laptops are reduced over their desktop counterparts due in part to the inability to keep the processors cool. Aside from the energy that is transmitted either as a signal or as light from a display, the preponderance of energy consumed by an electronic device is eventually released as heat energy. Therefore, the energy consumed by a device must be transferred from the device to its environment in order to maintain the temperature of the electronic device within acceptable operating limits. Managing this thermal load within the volume and form factors of standard portable devices has proven to be challenging. Most

computers for both desktop and portable configurations contain fans that serve to move air past the internal heat sources and carry the excess heat out to the environment. Fins and heat pipes are both used to carry heat away from the hottest internal elements to a location where the device might more readily exchange heat with the environment. In some devices, when the device is not expected to operate at full power for extended periods, materials with high thermal mass are included to absorb the heat put out by the device. The inclusion of this material will not change the maximum temperature reached at steady state, but it will delay the time it takes for the heat source to reach its maximum temperature. There are design options to mitigate the issues of thermal management, but it remains an important engineering consideration for portable electronic devices [17].

The problems of thermal management are exacerbated, however, by the use of a fuel cell in a portable power system. Due primarily to the relatively poor kinetics of the oxygen reduction reaction at the positive electrode, a fuel cell operating near its maximum power density (expressed in watts/cm^2 of cell surface area) will operate at approximately 50% efficiency. At 50% efficiency, a fuel cell that delivers 1 W of power to an electronic device will release 1 W of heat energy to its surroundings. Therefore, the device must transfer a total of 2 W to the environment. Assuming that a battery can deliver power at 80% efficiency, the battery system must dissipate 1.25 W of heat. By switching to a fuel cell, the thermal load is increased by 60%—a significant increase for a parameter that already limits system performance.

One could operate the fuel cell at lower current densities (increasing the operating cell voltage and consequently both increasing the efficiency and decreasing the amount of heat released by the cell) but in doing so, one would require a larger total area for the fuel cell stack. Thus, one would decrease the power density of the fuel cell. It remains a technical challenge to capture the increased energy density of a portable fuel cell while ensuring that the system remains within allowable operating temperatures.

9. Load handling

One must also consider the problem of load management and the ability of the system to react to changes in the amount of power demanded by the device. Portable power systems need to respond very quickly to changes in the load and they must be able to do so from a "cold start". Whether one is operating on hydrogen or methanol, one must be able to handle the transient that results from the time it takes for a fuel cell to reach its optimum operating temperature. This is not a bad problem under mild temperature conditions, but in extreme cold (sub-freezing conditions) this can be a significant barrier to performance. Also, if the system is completely dry, there is a time constant associated with

the hydration of the membrane. While the fuel cell will be able to produce some power from a dry start, it will take on the order of several seconds for the water generated at the cathode to diffuse across the membrane and provide it with sufficient hydration to produce power at peak levels. Either one must over-design the cell stack to ensure it can provide the power demanded of it under start-up conditions or one must include some auxiliary power system (i.e. a small rechargeable battery) to deliver the power while the fuel cell reaches its preferred operating conditions.

For a cell operating on methanol with control over the feed concentration, one would like to operate at a methanol concentration just above the minimum concentration necessary to ensure a given power output. If the power demand increases, then one must increase the methanol feed concentration to ensure that enough methanol can diffuse across the backing to meet the demand. When changing the power levels, however, one must allow for a transient after introducing the step increase in methanol concentration. The diffusion of methanol across a standard backing layer has a time constant on the order of 10 s, which means that the increased methanol concentrations will not reach the catalyst layer instantaneously. As with the case of starting up the cell, an auxiliary power source must be able to deliver power while the fuel cell responds to the changes demanded of it. The fuel cell can still be specified to handle all of the loads, but if one wants to optimize performance, it will be necessary to use a hybrid configuration, where the fuel cell handles most of the power and the battery handles only the transient loads.

The extreme limit of this hybrid configuration is one where a rechargeable battery handles all of the device loads and the fuel cell simply trickle-charges the battery to extend the time that the device can operate without an external recharge.[6] This approach then only adds complexity to a system without adding to the duration of a high-use duty cycle, because the trickle-charging approach demands that one have a long period of down time, during which the fuel cell can gradually recharge the battery, since the fuel cell will not necessarily provide sufficient power to operate the device itself.

10. System integration

Fuel cells do offer great promise for portable power systems, but one must deliver a complete system, not simply the stack itself. The system is sufficiently complicated that consideration of the fuel cell stack alone will not ensure a usable portable power source. By leveraging silicon (IC) manufacturing technology, we hope to develop a complete solution that includes the fuel cell, the fuel and oxidant distribution network and the monitoring and control electronics. Unlike conventional battery power systems, a fuel cell is not completely isolated from its environment. The system must take fuel and air as inputs and reject water and heat and the protocol for handling these inputs and outputs must be carefully considered.

11. Conclusions

One would like to take advantage of the energy storage density of a fuel cell to power portable electronic devices. Our design is implemented on a silicon substrate to leverage advanced silicon processing technology enabling optimal fuel cell performance and minimizing production costs. Aside from the complexity of construction, the bilayer design is a clear winner over the monolithic design.

In addition to optimizing the fuel cell stack operating performance, there are many system-level issues to be considered in developing a complete miniaturized power delivery system. These issues include air movement (oxidant supply), fuel delivery, water management, thermal management, power load management and system integration. The successful miniaturized power system will have considered each of these aspects and implemented engineering solutions appropriate for the particular system design. With the current state of technology, unless one is willing to relegate the fuel cell to a low-power device that simply extends the duration of the battery in the system by slowly charging it, these auxiliary system components limit the overall performance more than the design of the cell itself.

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[6] This external recharge can either be chemical (providing more fuel to the fuel cell) or electrical, provided that the device retains a means to recharge the battery from an external source. It should be pointed out that having an on-board trickle-charger in the form of a fuel cell only, helps with performance if the duty cycle is such that there are long "off" periods for the device between the high-drain periods, where the device is still removed from the external recharging source.

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