Miniature Fuel Processors for Portable Fuel Cell Power Supplies

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ABSTRACT

Miniature and microscale fuel processors are discussed that incorporate novel catalysts and microtechnology-based designs. The novel catalyst allows for methanol reforming at high gas hourly space velocities of 50,000 hr^{-1} or higher while maintaining a carbon monoxide levels at 1% or less. The microtechnology-based designs extremely compact and lightweight devices. The miniature fuel processors, with a volume less than 25 cm^3, a mass less than 200 grams, and thermal efficiencies of up to 83%, nominally provide 25 to 50 watts equivalent of hydrogen, which is ample for the portable power supplies described here. . With reasonable assumptions on fuel cell efficiencies, anode gas and water management, parasitic power loss, the energy density was estimated at 1700 Whr/kg. These processors have been demonstrated with a CO cleanup method and a fuel cell stack. The microscale fuel processors, with a volume of less than 0.25 cm^3 and a mass of less than 1 gram, are designed to provide up to 0.3 watt equivalent of power with efficiencies over 20%.

INTRODUCTION

Portable electronic technologies such as PDA's, notebook computers, and microelectrochemical systems (MEMS) have fueled a need for new, high-energy, small-volume power supplies for both military and commercial markets. Wireless electronic devices are currently limited to battery technologies, which, despite recent advances, are insufficient to provide the long-term power these new microelectronic systems require. A solution to this problem would be hybrid systems composed of a microscale fuel processor, proton exchange membrane fuel cells, and secondary batteries. Hybrid systems combine high-energy liquid hydrocarbon fuels (e.g., up to 12.4 kWhr/kg for diesel) with clean fuel cell power, and battery convenience. This paper summarizes work on hydrocarbon selection, fuel reforming catalyst development, and the progress of two fuel processing systems (25 to100 watts for soldier and personal portable power and 0.025 to0.500 watts for sub-watt power ranges). In addition to the fuel processor, these systems integrate two fuel vaporizers (one for the fuel processor and one for the catalytic fuel combustor); a catalytic combustor; and two heat exchangers, which preheat reactants and recuperate heat from product streams. This paper reports progress in these projects that has been made since the previous publications [1,2].
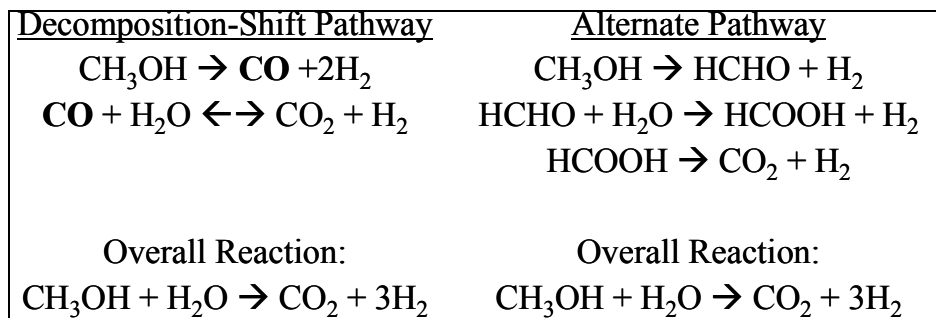
FUEL REFORMING

A wide range of hydrocarbon fuels such as methanol, ethanol, propane, butane, gasoline, and diesel are being reformed into hydrogen-rich streams for fuel cells. Diesel has the highest raw energy density; however, the raw energy density of the fuel does not necessarily translate to

the ultimate energy density of the device. For example, even though diesel has a raw energy density of 12.4 kWhr/kg, carrying enough water to operate at the stoichiometric steam to carbon ratio of 2:1 reduces its net energy density to 3.5 kWhr/kg. The net energy is also the same for methanol, with a stoichiometric steam to carbon ratio of 1:1.This reduction in net energy demonstrates the need for a water management system if a hydrocarbon-powered device is to reach its full energy density potential. It also shows that if no water management system is employed, methanol's lower reforming temperature makes it more desirable than diesel fuel for microelectronic applications. Methanol additional advantages include: it contains no sulfur; is available from renewable resources; and is completely miscible in water. For these reasons, methanol was selected as the initial fuel for use in developing the portable power supplies.

Battelle's proprietary methanol reforming catalyst is an important part of the portable power supply technology, because it is highly active, has a long life, and has a low selectivity to carbon monoxide. Over 99% methanol conversion has been achieved at relatively low temperatures (<350°C) and high gas hourly space velocities of 24,000-50,000 hr^{-1}. The catalyst was tested for 1000 hours with no detectable deactivation and was shown to be non-pyrophoric at room and low temperatures (<160°C). In addition, it has a low selectivity to carbon monoxide, which provides a product stream (reformate) with a CO content lower than equilibrium.

The ability of this catalyst to achieve lower than equilibrium concentrations of CO can be explained by looking at the steam reforming pathway [3]. Two alternative methanol steam reforming reaction pathways are shown in Figure 1. On the left side is a typical decomposition plus water-gas shift scheme. In this case, methanol first decomposes to CO and H_2, and then the CO reacts with H_2O to form CO_2 and more H_2. As the reaction proceeds, the minimum achievable CO content of the reformate is dictated by equilibrium constraints. At 350°C, this value is 5.4% CO in the dry reformate. On the right side of Figure 1, the pathway converts methanol to CO_2 and H_2 without producing CO. In this case, the minimum CO content of the reformate is dictated by the water-gas shift activity (or lack thereof) of the reforming catalyst. If there is very little shift activity, and the operating temperature is low enough to suppress the thermal decomposition of methanol, the CO levels can be kept well below the equilibrium concentration, which leads to the observed CO concentrations on the order of 1.0% and less (in dry reformate). Separate tests have confirmed that this methanol reforming catalyst has very little water-gas shift activity [4].

Decomposition-Shift Pathway	Alternate Pathway
$CH_3OH \rightarrow CO + 2H_2$	$CH_3OH \rightarrow HCHO + H_2$
$CO + H_2O \leftrightarrow CO_2 + H_2$	$HCHO + H_2O \rightarrow HCOOH + H_2$
	$HCOOH \rightarrow CO_2 + H_2$
Overall Reaction:	Overall Reaction:
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

**Figure 1.** Methanol reforming pathways.

SOLDIER PORTABLE POWER

Under a contract with the U.S. Army, Battelle is developing a hybrid power system designed to provide 15 to 25 watts of electric power for the dismounted soldier. This methanol-fueled system expected to provide up to 14 days of electric power before refueling. The final system will include an integrated microscale fuel processor, a proton exchange membrane fuel cell, and a rechargeable battery, and is expected to weigh less than 1 kg (excluding fuel). A representative system concept is shown in Figure 2. The device shown is based on hardware components, existing or being developed, capable of supporting a 15 to 25 W_e power supply. Larger power supply (50 W_e and 100 to300 W_e) systems are also being developed.

The major components of the fuel processor system have been thermally integrated into two different sizes of processors. The smaller device (volume of less than 20 cm^3 and mass less than 150 grams), Figure 3, has been demonstrated at reformate outputs from 8 to 39 watts electrical equivalent. The thermal efficiency was calculated by dividing the lower heating value of the hydrogen in the reformate stream by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor.

$$\eta_t = \frac{LHV_{hydrogen}}{LHV_{combustion\_meoh} + LHV_{refor\min g\_meoh}} \tag{1}$$
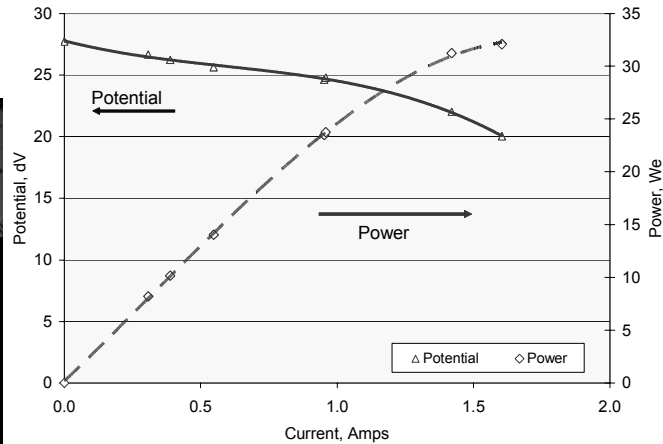
where LHV is the lower heating value.
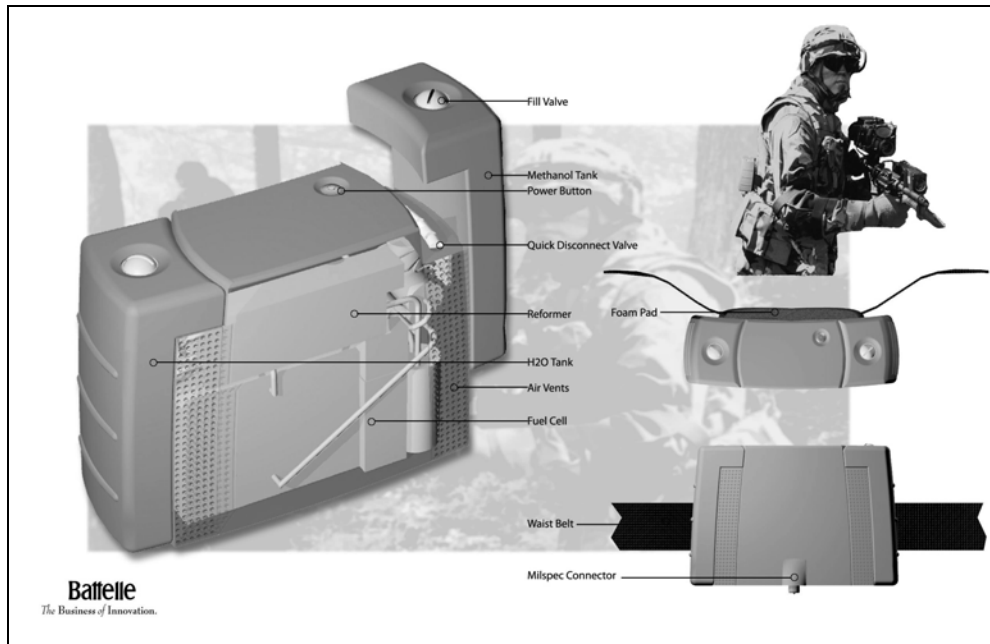
Figure 2. System concept for the soldier-portable power system.
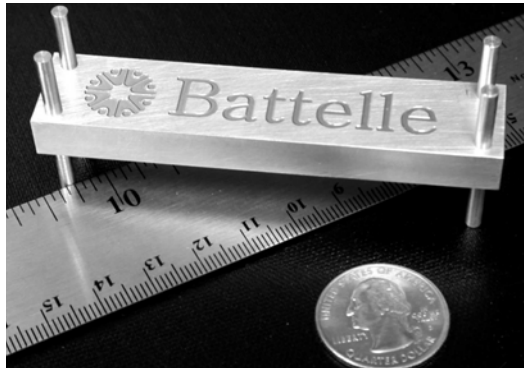
Figure 3. Integrated 15-25 W$_e$ fuel processor.

Figure 4. Fuel processor + carbon monoxide cleanup + H-Power fuel cell performance.

These performance numbers result in a thermal efficiency of 62% and a projected specific energy densities of up to 1500 Whr/kg, based on a 48% efficient fuel cell[1], a 1-kg device hardware weight, a 14-day mission, water recycle, anode gas recycle, and a parasitic power loss of 3W. The larger device, less than 25 cm^3 and 200 grams, has produced up to 54 watts electrical equivalent, with thermal efficiencies up to 83%. This results in higher energy densities of up to 1700 Whr/kg, based on a 48% efficient fuel cell[1], a 3-kg device hardware weight, a 14-day mission, water recycle, anode gas recycle, and a parasitic power loss of 5W.

For both units, typical gas compositions before CO cleanup were 72 to74% hydrogen, 24 to 26% carbon dioxide, and 1.0% or less CO on a dry gas basis. A CO cleanup unit was bread-boarded with the larger fuel processor, and CO levels less than 100 ppm were demonstrated. The cleaned reformate gas was fed to an H-Power fuel cell (Figure 4). This test validated the 48% efficiency fuel cell assumption and, more importantly, it demonstrated the feasibility of this approach.

SUB-WATT POWER

A miniature power supply is being developed that can provide 10 to 500 mW$_e$ power for microsensors, MEMS, and other autonomous microelectronics. Figure 5 shows the integrated microscale fuel processor, which has a volume of less than 0.25 cm^3 and a mass of less than 1 gram. The system incorporates two vaporizers/preheaters, a heat exchanger, catalytic combustor, and methanol steam reformer.

The fuel processor was operated over a wide range of conditions to obtain performance data. The operating temperatures required to achieve >99% conversion, 350 to 450°C, were higher than anticipated, and were attributed to the internal flow patterns, faster contact times than used in the catalyst screening tests, and thermal losses to the environment. The first- generation system produced between 18 and 100 mW$_t$ (based on the lhv) of hydrogen at a thermal efficiency of 3 to 9%. However, these efficiencies were considerably lower than reported above, because

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[1] Fuel cell efficiency assumes that 80% of the hydrogen fed to the fuel cell is reacted, and that the fuel cell converts 60% of the chemical energy to electrical energy. This gives a fuel cell efficiency of 80%*60%=48%.

the thermal losses as a percent of the thermal power out increase as with a decrease in thermal power out. The fuel processor was bread-boarded with a mesoscale high temperature (150°C) fuel cell (Figure 6), developed by Case Western University. This micropower system operated on methanol and was able to generate over 20 mW$_e$ of power (Figure 7).

The second-generation fuel processor has the same envelope and packaging as the original, but improves space utilization and thermal management. These improvements resulted in a decrease in operating temperatures from 350°C to 250°C while increasing the output and efficiency to 320 mW$_t$ and 23%, respectively. The CO also decreased from 1.8% to less than 1%, and under some operating conditions to less than 0.5%. The decrease in CO was attributed to the decrease in operating temperatures.
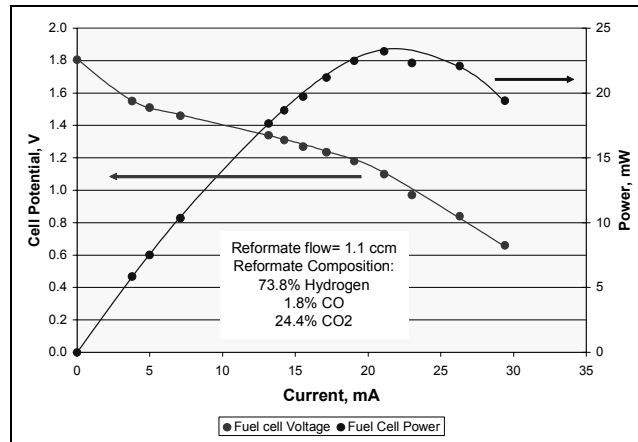
This second-generation processor will be further tested with a new mesoscale fuel cell. For the balance-of-plant components, state-of-the art insulation, pumps, and micro-valves are expected to be sufficient; however, for the gas delivery system, alternative designs are being developed.
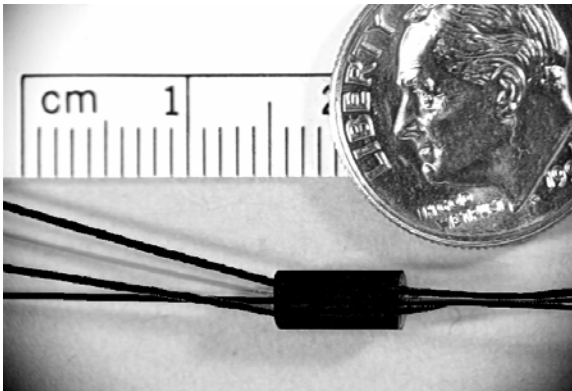
Figure 5. Microscale fuel processor
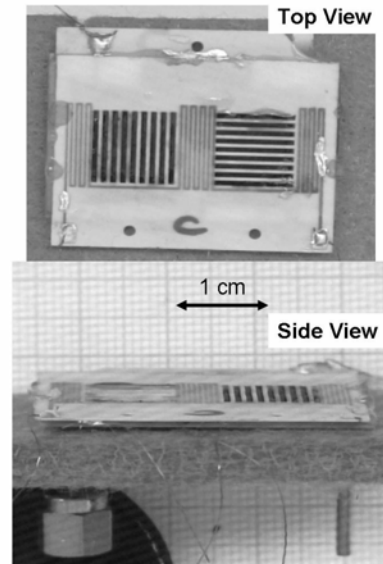
Figure 6. Mesoscale fuel cell

Figure 7. Microscale fuel processor and mesoscale fuel cell operation.

CONCLUSIONS

Lightweight, compact, power supplies are being developed that incorporate a microscale fuel processor, a fuel cell, and a secondary battery and deliver 25 to 300 watts of electric power. Miniature fuel processors, discussed here, have demonstrated 25 to 50 watts equivalent at high thermal efficiencies of up to 83% for an estimated energy density of up to 1700 Whr/kg. These processors have a volume of less than 25 cm^3 and a mass less than 200 grams. Initial tests with CO cleanup show a decrease in CO to less than 100 ppm, which is acceptable for many CO-tolerant fuel cells. A bread-boarded system composed of a Battelle fuel processor, a carbon monoxide cleanup unit, and an H-Power fuel cell has been demonstrated. Balance-of-plant components, such as pumps and blowers, have been identified and will be integrated in the next phase of testing.

A processor that can deliver less than 1 watt equivalent of hydrogen also has been demonstrated. The first-generation system had an efficiency of up to 9%. This system was tested with a mesoscale fuel cell and produced over 0.020 watts of electricity. An improved design (volume of <0.25cm^3 and mass of <1 gram) increased the power to 0.300 watts thermal (an increase of 50% over the original design) and the thermal efficiency to over 20%.

ACKNOWLEDGMENTS

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