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Microscale Power Generation Using a Fuel Processor and Fuel Cell

Jamie Holladay
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-373-1473, 509-376-5106, JD.Holladay@pnl.gov

Evan O. Jones
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-376-4610, 509-376-5106, Evan.O.Jones@pnl.gov

Max Phelps
Battelle, Pacific Northwest Division
902 Battelle Blvd
Richland, WA, 99352
509-375-6678, 509-372-4732, Max.Phelps@pnl.gov

ABSTRACT

A microscale fuel processor, which integrates a methanol steam reformer, catalytic combustor, vaporizers, and heat exchangers, has been designed, built, and tested. The methanol reforming reactor and catalytic combustor are less than 5 mm^3 in size each.

During testing, the processor converted a methanol water mixture (1:1 ratio by weight) into a hydrogen-rich stream composed of 73 to 74 vol% H_2, 25 to 26 vol% CO_2, and 0.6 to 1.2 vol% CO on a dry basis. Almost 3 moles of hydrogen were produced from each mole of methanol reacted in the reformer, which approached the theoretical maximum. The processor produced 0.1 to 1.1 sccm of a hydrogen-rich stream, which is equivalent to 18 to 135 mW_t. The reformer had a thermal efficiency of up to 9%.

When the reformer was integrated with a miniature fuel cell, the bread-boarded system produced up to 23 mW_e, which is the first time a micro-power system has generated electricity directly from a liquid fuel.

INTRODUCTION

Despite recent and expected advances in lithium-ion battery capabilities (Hossain 1995), the available energy densities do not solve the challenge of supplying extended, sustained power to microelectronic devices for remote and autonomous operation (Koeneman et al. 1997 and Harb et al. 2002). However, a new, microscale power supply system, based on thermal conversion of hydrocarbon fuels, has been shown to reach much higher energy densities than possible with current battery technology (Holladay et al. 2002). Table 1 shows a comparison of current practical battery technology and the thermal energy densities of some hydrocarbons.

TABLE 1. BATTERY ENERGY DENSITY VS. HYDROCARBON THERMAL ENERGY DENSITY

Technology	Energy Density, kW_e-hr/L	Energy Density, kW_e-hr/kg	Comments
Primary Cells			
Alkaline	0.330	0.125	
Zn-air	1.050	0.340	
$Li/SOCl_2$	0.700	0.320	
Secondary Cells			
Lead acid	0.070	0.035	
Ni-cad	0.055	0.035	
Ni-metal hydride	0.175	0.050	
Li-ion	0.200	0.090	
Li-polymer	0.350	0.200	Anticipated
Hydrocarbon	kW_t-hr/L	kW_t-hr/kg	
Methanol	4.384	5.6	Thermal energy
Butane	7.290	12.60	Thermal energy
Iso-octane	8.680	12.34	Thermal energy

(Adapted from Linden 1995)

Under a program funded by the Defense Advanced Research Projects Agency, Battelle, Pacific Northwest Division (Battelle) is developing a microscale power supply to provide between 10 and 500 mW_e for micro-electronic sensors and other micro-devices. This power supply consists primarily of a fuel processor to convert a liquid hydrocarbon to a hydrogen-rich stream, which is fed to a miniature fuel cell that reacts the hydrogen with oxygen from the air to produce water and electricity.

This technology combines a miniature fuel cell (1 to 2 cm^2) provided by Case Western Reserve University (CWRU) with a micro hydrocarbon fuel reformer. Since hydrocarbons have much higher energy densities than batteries (e.g., 5.6 kW_t-hr/kg for methanol and 12.6 kW_t-hr/kg for butane), converting the thermal energy in hydrocarbons to electricity with efficiencies even as low as 2% would result in devices with energy densities equivalent to current Li-ion batteries. The technology discussed here is targeting efficiencies of 5% or greater using hydrocarbon fuel sources. This paper focuses on the development of the fuel processor by Battelle, and its initial testing with a fuel cell provided by CWRU.

TECHNOLOGY DEVELOPMENT

A typical fuel processor is composed of five significant unit operations: fuel vaporizers/preheaters, fuel reformers, fuel clean-up unit(s), heat exchangers, and combustor. Additional components include pumps, blowers, valves, insulation, and other peripheral devices. Figure 1 is a schematic of a representative system. The challenge addressed by Battelle is to miniaturize and integrate the components into a microsystem.

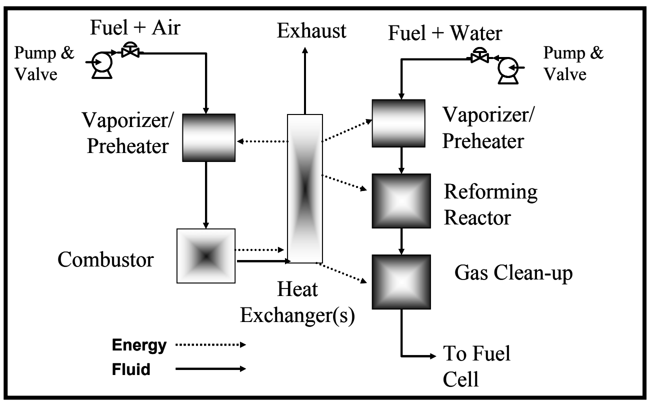

FIGURE 1. TYPICAL FUEL PROCESSOR SCHEMATIC

Battelle is a leader in the development of miniature reactors (Palo et al. 2002; TeGrotenhuis et al. 2000; and Tonkovich et al. 1999), and holds patents in this area (see, for example, Wegeng et al. 1997 and Wegeng et al. 1998). We have developed and applied this technology to miniature chemical reactors, heat exchangers, and other chemical and physical processes, as well as equipment with characteristic dimensions on the micrometer scale. Figure 2 illustrates the different characteristic size ranges for different applications.

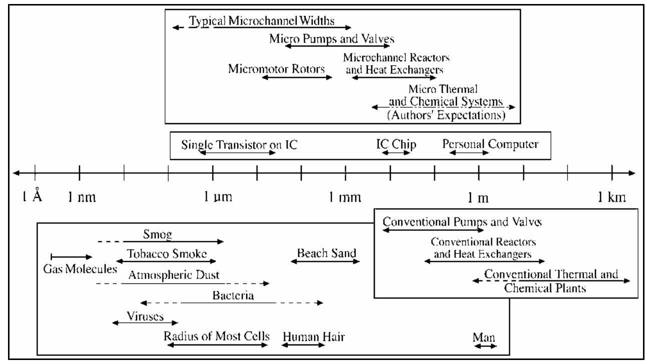

FIGURE 2. CHARACTERISTIC SIZES OF COMMON SYSTEMS

Critical issues in developing integrated micro-power fuel processor and fuel cell systems include minimizing heat loss, minimizing the requirement for processing water, and packaging or balance of plant. Methanol is the optimum fuel for micro-power systems, because it has a low operating temperature and minimizes heat loss. Methanol also minimizes the requirement for processing water.

For a miniature power supply, such as discussed in this paper, all the water needed for the steam reforming would likely be carried on the system. Table 2 describes energy densities of hydrocarbon plus water. In larger power supplies, it is feasible to recycle water; however, the added complexity, components, and control elements make this approach impractical for this small scale. The methanol/water mixture has an energy density greater than that of the other hydrocarbon/water mixtures.

TABLE 2. FUEL PROCESSOR FEED ENERGY DENSITY (HYDROCARBON + WATER)

Fuel	Steam to Carbon Ratio	Energy Density kW_t-hr/L	Energy Density kW_t-hr/kg	Reforming Temp. (°C)
Methanol	1	2.810	3.290	300-400
n-Butane	2	2.570	3.110	450-650
n-Octane (gasoline)	2	2.670	2.990	550-750

EXPERIMENTAL

The integrated unit, composed of two vaporizers/preheaters, a heat exchanger, catalytic combustor, and methanol steam reformer, is shown in Figure 3. The reformer has a volume of less than 5 mm^3 and a capacity of 200 mW_t. The combustor volume, also less than 5 mm^3, has a capacity of up to 3 W_t. For the experiments, the oversized combustor capacity allowed a wide range of operating conditions to be examined. The combustor fuel was either hydrogen or methanol. A detailed description of the setup is provided elsewhere (Holladay et al. 2002).

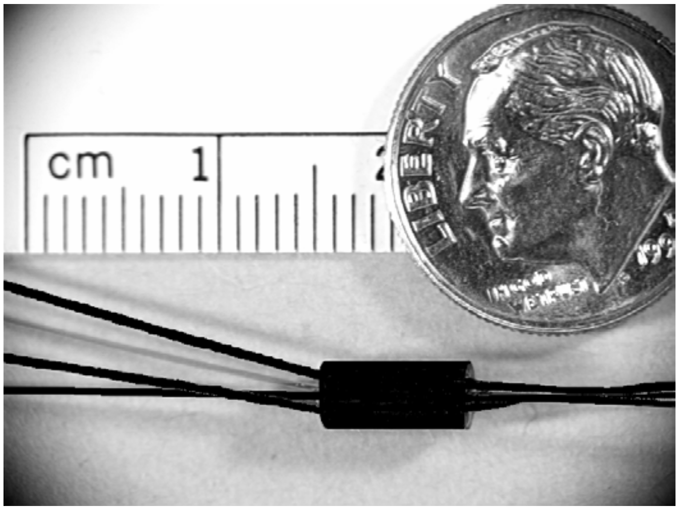

FIGURE 3. INTEGRATED MICROFUEL PROCESSOR

The test stand consisted of syringe pumps, gas controllers, vapor liquid separation units, and an online gas chromatograph. Syringe pumps fed the methanol/water mixture to the reformer at rates of 0.02 cc/hr to 0.1 cc/hr (20°C basis), and pure methanol to the combustor at rates of 0.1 cc/hr to 0.4 cc/hr (20°C basis). Air was fed to the combustor at rates between 8 and 20 sccm. The product gases (reformate) were fed, via a dri-rite tube to eliminate any residual water vapor, to an online micro gas chromatograph (Agilent QuadH) for analysis or to a fuel cell. The processor was able to be started without electric heating by initially feeding hydrogen gas to the combustor and then, once above 70°C, slowly reducing and eliminating the hydrogen flow and slowly increasing the methanol feed.

The fuel cell in this work was developed at CWRU using their polybenzimidazole (PBI) technology. This type of technology offers the potential of higher carbon monoxide tolerance than found in conventional proton exchange membrane fuel cells (Gervasio et al. 2002). This ability to tolerate higher levels of carbon monoxide simplifies the processor system significantly, as at least two carbon monoxide cleanup reactors can be eliminated (Holladay et al. 2002).

The CWRU fuel cell consisted of two cells in series, with each cell having an area of ≈1cm^2 designed to provide up to 100 mW$_e$. A series of thick-film printing steps were used to deposit current collectors, heaters, and a Pt RTD on alumina. The heaters were necessary to allow the cells to be tested at the appropriate temperature. Eventually, packaging the fuel cell with the fuel processor unit is expected to allow the heaters to be eliminated altogether. The RTD allows the fuel cell temperature to be monitored and the heaters controlled.

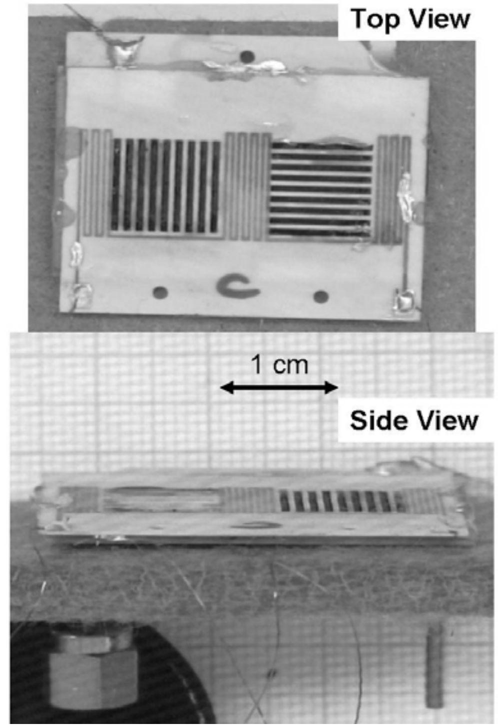

FIGURE 4. CWRU FUEL CELL

RESULTS AND DISCUSSION

Fuel Processor

The fuel processor was operated over a wide range of conditions to obtain performance data. To achieve >99% conversion, 350-450°C operating temperatures were required. These temperatures 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 operating conditions and results are summarized in Table 3. The hydrogen flow from the reactor ranged from 0.1 to 1.1 sccm, which corresponded to a thermal power between 18 and 200 mW$_t$. For an ideal system (all the carbon going to carbon dioxide), the ratio of hydrogen gas produced to methanol reacted would be 3. In this system the ratio was 2.7 to 2.8, depending on the conditions, indicating that the reactor was performing well.

The thermal efficiency ranged from 3% at 18 mW$_t$ to 9% at 200 mW$_t$. 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.

$$\eta_t = \frac{LHV_{hydrogen}}{LHV_{combustion\_meoh} + LHV_{reforming\_meoh}}$$

where LHV is the lower heating value.

The low thermal efficiency was caused by the relatively high thermal losses to the system. To reduce the losses a new device with smaller and fewer inlet and outlet tubes is being designed. The effect of vacuum packaging on the system will also be tested in the next generation of processors.

TABLE 3. DEMONSTRATION OPERATING CONDITIONS AND RESULTS

Operating Conditions	
Reformer temperature	350-450°C
Pressure	1-2 psig
Water/methanol molar ratio	1.8
Fuel Processor Results	
Methanol conversion	>99%
Typical gas composition	
Hydrogen	73.8%
Carbon dioxide	24.4%
Carbon monoxide	1.8 %
Hydrogen production	18-135 mW_t
Methanol fed to the system	600-1500 mW_t
Fuel processor thermal efficiency	3-9%

Fuel Processor and Fuel Cell

The 1.1 sccm of reformate gas was fed to the CWRU fuel cell. The fuel cell was electrically heated to approximately 150°C using the built-in electric heaters, requiring 120mA at 31V for a power of 3.7W_e. A variable load was applied to the fuel cell, and the resulting performance is presented in Figure 5. A maximum power output of 23 mW_e was produced, and the fuel reformer and fuel cell system efficiency of 0.46% was achieved. The efficiency was calculated by dividing the power out of the fuel cell by the thermal power of the methanol fed to the combustor and steam reformer plus the electric power used to heat the fuel cell.

$$\eta_t = \frac{FC\_Wattage}{LHV_{combustion\_meoh} + LHV_{reforming\_meoh} + W_{FC\_e}}$$

where LHV is the lower heating value and W_{FC_e} is the electric power to heat the fuel cell.

CWRU was able to operate the same fuel cell, using hydrogen gas feed, with only 2 W_e of electric power supplied to the heater, while, inexplicably, more power 3.7 W_e was required when the cell was operated at Battelle. If only 2 W_e is required, the system efficiency increases to 0.7%. The low power output from the fuel cell was ascribed to the carbon monoxide tolerance of the fuel cell being lower than expected. The tolerance could be increased by raising the fuel cell temperature and by hydrating the stream. These tests will be conducted with the next generation of processors.

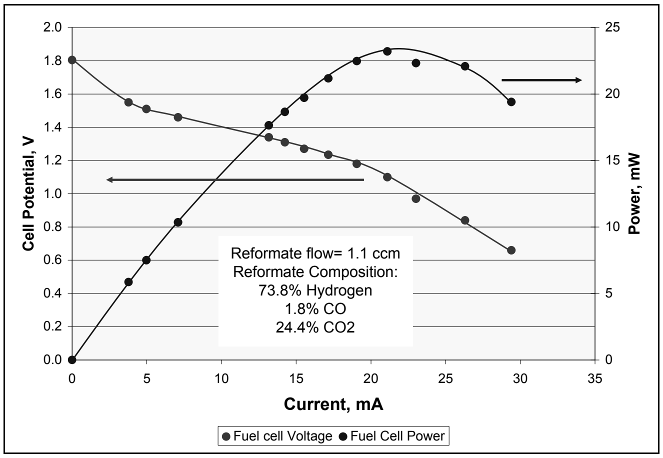

FIGURE 5. BREAD-BOARDED FUEL PROCESSOR AND FUEL CELL PERFORMANCE

CONCLUSION AND FUTURE WORK

A high-energy power supply is being developed that provides more extended operating times and efficiencies for microelectronic devices than conventional battery technologies. An integrated methanol fuel reformer system has been designed and built. Testing of the integrated fuel processor system resulted in the production of 135 mW_t of hydrogen at a thermal efficiency of 9% utilizing methanol as fuel. The reformate stream was composed of 73 to 74% hydrogen, with 25 to 26% carbon dioxide and carbon monoxide constituting the rest. The device approached the ideal conversion ratio of 3 moles hydrogen produced per mole of methanol reacted.

Electricity was produced using methanol fuel by integrating the micro-fuel processor with a fuel cell. The bread-boarded system produced 23 mW_e of electricity at an efficiency of 0.46%.

Development of both the fuel processor and fuel cell will continue. The thermal integration of the fuel cell and processor should increase the overall efficiency, as will improvements in the processor and cell designs. A complete system would consist of liquid and gas delivery systems, valves, packaging, and integration with a fuel cell.

ACKNOWLEDGMENTS

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REFERENCES

Gervasio, D., S. Rogers, R. Koripella, D. Zindel, and S. Samms, 2002, "Elevated Temperature Fuel Cells for Portable Power Applications," *Topical Conference Proceedings, American Institute of Chemical Engineers - Fuel Cell Technology: Opportunities and Challenges,* G.J. Igwe et al., ed. AICHE Pub. No. 161, pp. 473-474.

Harb, J. N., R. L. LaFollette, R. H. Selfridge and L. L. Howell, 2002, "Microbatteries for Self-Sustained Hybrid Power Supplies," *Journal of Power Sources*, Vol. 104, pp. 46-51.

Holladay, J. D., E. O. Jones, M. R. Phelps, and J. Hu, 2002, "Microfuel Processor for Use in Miniature Power Supply," *Journal of Power Sources*, Vol. 108, Issue 1-2, pp. 21-27.

Hossain, S., 1995, "Rechargeable Lithium Batteries (Ambient Temperature)," *Handbook of Batteries,* D. Linden, ed. McGraw-Hill, Inc., New York, 1995, p. 36.1

Jones, E. O. J. Holladay, S. Perry, R. Orth, B. Rozmiarek, J. Hu, M. Phelps, and C. Guzman, 2001, "Sub-Watt Power Using an Integrated Fuel Processor and Fuel Cell," *Proceedings, 5th International Conference on Microreaction Technology,* M. Matlosz et al., ed. Springer-Berlin Germany, pp. 277-285.

Koeneman, P. B., I. J. Busch-Vishniac, and K. L. Wood, 1997, "Feasibility of Micro Power Supplies for MEMS," *Journal of Microelectromechanical Systems,* Vol. 6 No. 4, pp. 355-362.

Linden, D., 1995, "Selection and Application of Batteries," *Handbook of Batteries, 2nd edition,* D. Linden, ed. McGraw-Hill, Inc., New York, pp. 6.5.

Palo, D. R., J. D. Holladay, R. T. Rozmiarek, C. E. Guzman-Leong, Y. Wang, J. Hu, Y. Chin, R. A. Dagle, and E. G. Baker, 2002, "Development of a Soldier-Portable Power Fuel Cell Power System, Part I: A Bread-Board Methanol Fuel Processor," *Journal of Power Sources*, Vol. 108, Issue 1-2, pp. 28-34.

Palo, D. R., J. D. Holladay, R. T. Rozmiarek, C .E. Guzman-Leong, Y. Wang, J. Hu, Y.-H. Chin, R .A. Dagle, and E. G. Baker, 2001, "Fuel Procesor Development for a Soldier-Portable Fuel Cell System," *Proceedings, 5th International Conference on Microreaction Technology,* M. Matlosz et al., Springer-Berlin Germany, pp. 359-367.

TeGrotenhuis, W. E., R. S. Wegeng, D. P. VanderWiel, G .A. Whyatt, V. V. Viswanathan, and K. P. Schielke., 2000, "Microreactor System Design for NASA In situ Propellant Production Plant on Mars." *AICHE 2000 Spring National Meeting*, Atlanta, Georgia,.

Tonkovich, A. Y., J. L. Zilka, M. J. Lamont, Y. Wang, and R. S. Wegeng, 1999, "Microchannel Reactors for Fuel Processing Applications. I. Water Gas Shift Reactor," *Chem Eng Sci.*, Vol. 54, pp. 2947-2951.

Wegeng, R. S., M. K. Drost, and C. E. McDonald, US Patent No. 5 611 214 (1997).

Wegeng, R. S., M. K. Drost, C. J. Call, and J. G. Birmingham, C. E. McDonald, D. E. Kurath, M. Friedrich, US Patent No. 5 811 062 (1998).

Whyatt, G. A., W. E. TeGrotenhuis, J.G.H. Geeting, J. M. Davis, R. S. Wegeng, L .R. Pederson, 2001, "Demonstration of Energy Efficieny Steam Reforming in Microchannels for Automotive Fuel Processing," *Proceedings, 5th International Conference on Microreaction Technology,* M. Matlosz et al., ed. Springer-Berlin Germany, pp. 303-312.