PORTABLE DIRECT METHANOL FUEL CELL SYSTEMS

S. R. Narayanan* and T. I. Valdez

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

***All correspondence to be addressed to:**
s.r.narayanan@jpl.nasa.gov
Telephone: (818) 354 0013
Facsimile: (818) 393 6951

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Abstract

The simplicity of the direct electro-oxidation of methanol in a polymer electrolyte membrane fuel cell and the technological advances achieved in performance and efficiency in the last ten years has spurred the development of DMFC-based portable power systems in the power range of 0.1 – 150 Watts. Most of the system demonstrations to date have focused on proving the feasibility of novel stack designs, membrane types, integrated system configurations, and miniaturization concepts. This article includes discussion of the specific power and power density requirements for various portable system applications, the status of stack technology, progress in the implementation of balance-of-plant designs, and a summary of the characteristics of various DMFC portable power source demonstrations. Compact monopolar and bipolar designs being demonstrated at various power levels. Integrated systems at the 25-150 Watt level have demonstrated functionality for multipurpose power source applications for the military and commercial area, although these demonstration present substantial scope for weight and volume improvements. Efforts in the power range of 0.1-15 Watts have focused on size and mass, as these are premium requirements for the small portable consumer electronics market. Recent demonstrations relate to lightweight stack configurations while closed loop systems with water recovery and thermal management are at best in the initial phases of demonstration.

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1.0 Introduction

The advantages of methanol as a high-energy fuel and the system simplicity offered by the process of direct oxidation at ambient temperatures makes the direct methanol fuel cell an excellent candidate for portable power systems. The theoretical energy content of methanol is approximately 6000 Wh/kg. Hydrogen storage systems even with 10 % storage (by weight) can only offer a theoretical energy content of 3200 Wh/kg. Methanol ~~being~~ is a liquid fuel that can be transported at ambient pressures as a pure liquid or as an aqueous solution. Thus, methanol can be deployed in a consumer environment with little concern, and portable power systems that can be refueled by the consumer from a disposable cartridge or fuel bag are conceivable. Issues with transportation and handling of hydrogen in a consumer environment have always presented grave concerns, and methanol is certainly perceived to be significantly safer than hydrogen. However, risks arising from widespread methanol use will require new safeguards and regulations. From a technology viewpoint, the direct oxidation of methanol in a fuel cell is a much simpler system compared to those indirect hydrogen-air fuel cell systems that require fuel processing to generate hydrogen. Also, the technological advances in performance and efficiency of direct methanol fuel cells achieved in the last ten years have led to the

design of several prototype demonstration units by various organizations. Most of the system demonstrations to date have focused on proving the feasibility of novel stack designs, membrane types, integrated system configurations, and miniaturization concepts.

2.0 Requirements for Portable Systems

Portable DMFC power systems are being considered for mobile phones, personal wireless devices, laptop computers, military communication systems, multipurpose emergency power sources, robotic devices, and healthcare systems for mobility and life support. These applications are characterized by significant differences in power output, mass and volume. Typical power levels considered for portable systems range from 100 mW - 500 Watts and the approximate size and mass constraints for several candidate applications are shown in Table 1.

Insert Table 1 here

The application information in terms of power density and specific power requirements for a fuel cell system is shown in Figure 1.

Insert Figure 1 here

Figure 1 is an attempt to normalize the needs for the various applications and examine differences and overlapping requirements. For example, multipurpose/emergency power sources and personal mobility and life support systems are noted to have very similar power requirements. Laptop and the soldier power source make volume requirements a challenge while mobile phones are more demanding on weight than the laptop power source. From the viewpoint of power, cellular phone chargers are the least demanding of

all applications while power systems for mobile rovers present the most significant challenges. The power source characteristics in Table1 and Figure 1 determine the power density requirements for the fuel cell stack, power demand by ancillary sub-systems, fuel efficiency, and choice of system configuration. In addition to satisfying these principal electrical demands, the product design will also have to meet other requirements associated with fuel handling, product disposal and operation in extreme environments. While the DMFC is a candidate for all the applications in Table 1, only in some applications can all the requirements be readily addressed by state-of-art technology. In other cases, two to three times improvement in technology characteristics would be needed to optimally satisfy all the requirements. The emerging need for portable sources that can provide long operating times and freedom from electrical re-charging is currently urging further development.

3.0 Fuel Cell Stack and Ancillary System Requirements

The technology characteristics of the fuel cell stack and the balance-of-plant determine the properties of the portable power source. Cell power density and stack design determine the fuel cell stack specific power, while system efficiency and system configuration type determine the balance-of-plant characteristics. In Figure 2, the specific power of the fuel cell stack and the weight of balance-of-plant required to support the generation of a certain amount of power (expressed in W/kg) are plotted.

Insert Figure 2

Each of the lines in Figure 2 represent the outer edge of the technology characteristic envelope that the stack and balance of plant must jointly satisfy or exceed in order to realize a power source for the specific application in Table 1. These lines are independent of the system efficiency as the weight of fuel is not included in any of these calculations. For example, to realize a 25 Watt power source that weighs 1 kg, the fuel cell stack with a specific power of 40 W/kg must be combined with a balance-of-plant that has the characteristic of supporting 60W/kg. Similar envelopes can be created with volume parameters as well. Such plots help determine the technology goals in the area of stacks and balance-of-plant for various portable DMFC systems. The status of the technology with respect to the stack and balance of plant are now discussed so that we may understand the applications that can be readily addressed by the state-of-art technology.

4.0 Stack Technology Status

With a single cell operating at 0.45V at 150 mA/cm^2 and with state-of-art bipolar plate stacking technology, the power density under realistic system operating conditions (55°-60°C, ambient pressure air operation) is approximately 55 W/kg. While it is not unusual to find higher power densities reported for DMFC stacks, it is important to qualify the stack properties under operating conditions that are consistent with the realization of overall thermal balance and water balance for the system. Such a qualification usually results in reduced values of specific power. Stack designs of the type shown in Figure 3 have been developed jointly by the Jet Propulsion Laboratory and Giner Inc. and have been validated under system operating conditions.

Insert Figure 3 here

In this stack air is supplied from a plenum and flows through wide channels in a direction perpendicular to the flow of methanol solution. The pressure drop on the cathode side is less than 0.2 cm of water. When operated at 55°C on ambient pressure air, at airflow rates of about 1.7 times the stoichiometric, the water and thermal balance requirements of a system are met. A 200 watt stack of this type is expected to weigh 3.6 kg.

Yet another stack design from Los Alamos National Laboratory has been operated and the design was validated as part of a 50 Watt system integrated by Ball Aerospace Corporation. This 30-cell stack had a cell active area of 45 cm^2 and when operated at 60°C and 0.45 V/cell had a power output of 78 Watts exhibited a specific power of 31 W/kg and a power density of 78 W/liter. This particular bipolar stack design was considered extremely conservative with substantial scope for weight reductions. A photograph of this stack is shown in Figure 4.

Insert Figure 4 here

For handheld applications such as mobile phones, because of user comfort requirements the preferred operating temperature for the stack is close to ambient temperature, and typically not more than 35°C. At these low operating temperatures, the specific power of conventional bipolar plate stack designs reduces to about 20 W/kg. From Figure 2, it can be concluded that employing a DMFC stack with a specific power of 20W/kg for a

portable phone application requires that the balance of plant characteristics need to be in excess of 100 W/kg. Thus realizing a cellular phone power source places a tremendous demand in the reduction of the weight of the balance-of-plant unless the specific power of the stack can be raised substantially. This situation has prompted the development of lightweight stack designs. The weight of the biplates and endplates is usually 80-90% of the stack mass in conventional stacks. Biplates are crucial in minimizing voltage losses when operating at high stack currents. However, when the actual currents flowing through the stack are small, higher cell impedance configurations may be acceptable. This would be an attractive trade-off especially if significant weight reduction can be accomplished with an acceptable stack impedance. Such a compromise is readily achieved in monopolar configurations where the current is collected along the edges, or in the plane of the electrodes and bipolar plates are eliminated [1]. Challenges of designing monopolar stacks rest in minimizing orientation insensitivity, water removal and achieving good sealing. Such monopolar stacks that provide 50 Watts/kg operating at 35°C have been developed at the Jet Propulsion Laboratory.

5.0 Balance-of-Plant Technology Status

The balance- of- plant for a DMFC systems consists of the heat exchangers, pumps, sensors, gas-liquid separator, methanol concentration sensor, control electronics and the power management sub-system.

Insert Figure 5 here

In Figure 5 the balance-of-plant is enclosed in the two large rectangles. Since concentration of methanol in the fuel circulation loop influences the power density, crossover rate and efficiency, a methanol concentration sensor is very important part of the control system of the direct methanol fuel cell. The Jet Propulsion Laboratory has developed an electrochemical sensor that has been operated for extended periods as part of an automated feedback and control system [2]. The sensing principle is based on the measurement of the diffusion-controlled current for the electro-oxidation of methanol in a polymer electrolyte membrane cell at a platinum-ruthenium electrode.

Stacks with low pressure drop on the air side and liquid side are needed to reduce parasitic losses. Airflow rates determine the domain of thermal and water balance for the system. Therefore, it is important to operate at as low an airflow rate as possible so as to minimize or eliminate water recovery by condensation to avoid increase of the weight of the balance of plant. By operating at airflow rate of 2 times the stoichiometric requirement or less, the need for water recovery by condensation can be avoided even at an ambient of 42°C and 0% relative humidity. Permissible airflow rates and methanol concentration also limit the operating temperature of the stack and hence the maximum stack power attainable in a system configuration. Water transported from the anode to the cathode by electro-osmosis must be returned to the anode in order to maintain water balance. Methanol crossover has a significant impact on the size of the thermal and water management system and the resources demanded by the balance of plant, and hence membranes that can improve the fuel efficiency beyond 90% are important to minimizing the overall system size and mass.

Start-up of the stack can be achieved as long as reactants are made available to the stack. A small rechargeable battery would be necessary to perform the start-up and control functions initially. However, to extend operation over a wide range of ambient temperature below 0°C, additional energy would be required in batteries. A balance-of-plant design by the Jet Propulsion Laboratory that allows system operation with instant start-up to full power between 15°C and 42°C and employing off-the-shelf components is estimated to be about 5 kg for a 150-Watt system. This translates to about 30 Watts of power generation supported by every kilogram of balance-of-plant.

6.0 System Characteristics

Given the technology characteristics of 50W/kg for the stack and 30 W/kg for the balance-of-plant, it is seen from Figure 1 that a 100 Watt power source that weighs 5 kg can be realized. The overall power density of conventionally built DMFC systems could therefore aim at being 20W/kg. The balance of plant for a typical DMFC system is expected to take up 15% of the power generated by the stack. Given the operating point of 0.45-0.5V /cell and a fuel efficiency of 85%, this translates to an overall system efficiency of about 26-29%.

According to Figure 2, the 2-Watt portable phone power system that weighs 100g should also be realizable. However, the internal stack temperatures of 55°C, and temperature of air exhaust could be challenges to product design. To operate at lower stack operating temperatures lightweight stack designs would be essential. Also, miniature fluid handling

systems would be necessary to attain the balance-of- plant characteristics required for handheld compact systems.

An advanced 100 Watt hydrogen-air fuel cell power system developed by Ball Aerospace has a specific power of 27 W/kg [3]. When a portable power source with a capability of 5000 Wh is considered, such a hydrogen-air system would have a total weight (system and pressurized hydrogen fuel at 3000 psig included) of 10 kg. The direct methanol fuel cell system with the same capacity and operating at a system efficiency of 20% would weigh about 9.1 kg. While more efficient hydrogen storage options are being developed, it is clear that at the current state of technology, direct methanol fuel cell systems with comparable energy and power densities to the hydrogen-air systems, can be realized when fuel supply is considered part of the power source package.

7.0 System Demonstrations

In the last three years, portable systems based on DMFC technology have been demonstrated in the range of 25-150 Watts and also at the low wattage level of 0.1-15 watts. The characteristics of these demonstration units will now be discussed.

25-150 Watt systems:

At least four system units listed in Table 2 have been demonstrated in 2001-2002. While some characteristics are in the public domain, in almost all cases extensive data on performance is not available at this time.

Insert Table 2 here

The characteristics listed in Table 2 suggest that three of the systems other than the 40 W system claimed by Smart Fuel Cell Inc, fall short of meeting the power density and specific power desired for the multipurpose power source applications. From discussions with all the respective organizations it appears that there is considerable scope for reduction in the weight and volume of the units and the focus in these efforts was primarily demonstrating system functionality at a various levels.

The 50-Watt DMFC system shown in Figure 6 was developed by Ball Aerospace system for DARPA. The system uses a 1.9 kg stack based on Nafion membranes fabricated by Los Alamos National Laboratory. An in-line methanol concentration sensor controls concentration of methanol. This arrangement allows the loads to be varied readily and ensures optimal efficiency at all times. The unit includes active water recovery with capability of operating at 40°C at 0% relative humidity, and has provisions for electrical heating from an external power source if required to start up when frozen. During limited testing, methanol to electric efficiencies as high as 30% has been observed under full load. Current efforts focus on 20-Watt system that incorporates a lightweight 400 g stack from Los Alamos National Laboratory.

One of the key features of the 150-Watt system developed by Giner Electrochemical Systems Inc., shown in Figure 7 is that it demonstrates a proprietary low crossover membrane that offers about 60% reduction over Nafion 117 with no loss of performance.

Insert Figure 7 here

The stack and system have been operated for about 120 hours. The system includes active water recovery. Methanol concentration control in the feed loop is maintained by monitoring the consumption rate measured by the number of ampere-hours drawn. This type of control would be ideal for steady state operation and where the efficiency does not fluctuate, however will require periodic re-adjustment of methanol concentration. The system requires 2 minutes to reach full power output. A 75 Watt unit is currently under development and is expected to have twice the power density of the 150 Watt unit.

Smart Fuel Cell Corportation has demonstrated a 25 Watt complete system that includes a 2.5 liter cartridge sufficient for 100 hours of operation (Figure 8a).

Insert Figure 8 here

The system is capable of instant start up as it is equipped with a 40 Wh battery that is kept charged by the fuel cell. This type of hybrid configuration allows transiently high loads of up to 80Watts to be imposed on the system. The battery also enables instant system start up at ambient temperatures as low as –20°C. This system exemplifies the benefits of a hybrid design. With active water recovery, similar to the other systems discussed, operation can be ensured at ambient temperatures as high as + 40°C and 0% relative humidity. Methanol utilization values suggest an overall system efficiency of about 21%. Smart fuel cells has also demonstrated a 40 Watt system (Figure 8b) with

substantially reduced weight of 1.9 kg that is anticipated to be available commercially in 2003.

Low Wattage Fuel Cells (0.1 Watt –15 Watts)

The development of low-wattage fuel cells has been directed at cellular phones, personal digital assistants, laptops and other personal electronic devices that require long operating times and where freedom from recharging of batteries is desired. The developments in this area have largely focused on demonstrating cell configurations, stack designs and miniaturization of balance-of-plant. In this category, systems that are thermally balanced and perform water recovery have not been developed and leave much to be desired in the way of complete power systems. These efforts clearly assert the challenges in the miniaturization of stacks and balance-of-plant. Some of the recent developments are now described.

Manhattan Scientifics has been developing a direct methanol fuel cell for charging cellular phone batteries thereby increasing the standby time. The fuel cell is a monopolar cell design that involves connecting an array of over a couple of dozen cell elements sputter-deposited on a single polymer electrolyte layer[6]. These cell layers are arranged to provide a compact flat package that is amenable to rapid manufacturing. The power densities in this type of design is < 1 mW/cm^2 and methanol delivery is controlled by slow diffusion from an ampoule. The total power output for these fuel cell systems is approximately 100mW . At this power level, operation of a cellular phone in talk mode

cannot be supported. However slow re-charging of batteries and standby operation are the preferred applications of this DMFC system.

In June 2001, Motorola Inc. integrated a direct methanol fuel cell system with an output of 100 mW. The system included balance-of-plant that supported fluid flow management, concentration control, methanol delivery and control electronics. The system was operated on passive air with no water recovery for 6 days. Motorola has used in-house capabilities in low-temperature co-fired ceramic packaging technology for the fabrication of the microfluidic structures. The cells were fabricated with Nafion membranes and four cells were connected in series to form a flat module [7]. Motorola is expecting to incorporate active recovery of water transported from anode to the cathode in future designs which are being designed to deliver higher power levels. Another key issue being addressed is the high parasitic power demand by the balance-of-plant [7].

The Jet Propulsion Laboratory (JPL) has been focusing on increasing the power density of direct methanol fuel cell stacks so that a wide range of portable power applications can be addressed with stacks operating near ambient temperatures. To this end JPL has demonstrated a new flat-pack monopolar configuration that integrates several cells on a single polymer electrolyte layer and provides substantial weight reduction for the DMFC stack[1]. Efficient stacking configurations with back-to-back electrodes of the type shown in Figure 9, that allow for at least two to three times improvement in stack specific power over conventional bipolar stack designs have been demonstrated.

Insert Figure 9 here

In March 2002, JPL demonstrated a 5-Watt direct methanol fuel cell system that uses a lightweight monopolar stack (Figure 10). The cell power densities as high as 35 mW/cm^2 was demonstrated at 30°C operating on ambient pressure airflow supported by natural convection. When operated at 60°C, this stack is expected to have a specific power of 120 W/kg, demonstrating that weight reductions can be realized by adopting a monopolar stack design. This system is operated on dilute 1.5 M methanol. The unit is approximately 15 cm x 10 cm x 7.5 cm and is capable of powering several cell phones.

Insert Figure 10 here

Lynntech Inc., has developed a 15-Watt direct methanol fuel cell system shown in Figure 11.

Insert Figure 11 here

The system employs a stack based on a monopolar design [8]. The stack power density reported is approximately 75 W/kg, demonstrating benefits of a monopolar stack design. The system operates on 4 molar methanol as fuel and when the power output drops is refueled with fresh 4 molar solution. The balance of plant mass has not been optimized

and thus the system power density of 10W/kg that was realized has considerable scope for improvement. The system has been operated intermittently for about 200 hours.

8.0 Conclusions

Based on the state of development of direct methanol fuel cell systems, it is anticipated that early market entry would be in the power range 25-150 Watt, because of the relative maturity of the system demonstrations and the less demanding power characteristics for multipurpose and military applications. The consumer electronic devices of the future that are likely to be "always on" would increase the need for power sources that offer freedom from recharging of batteries. The need for power characteristics of 20 W/kg and 20 W/liter for small portable consumer electronics places a strong emphasis on miniaturization and weight reduction in the future. A hybrid configuration with DMFC and a rechargeable battery is most likely to fill the application demands with respect to power density and start up, before "fuel cell only" systems are progressively miniaturized. Trace methanol emissions from the carbon dioxide exhaust of DMFC must be catalytically combusted before release into the environment to avoid exposure to methanol in confined environments. The risks of widespread use of methanol as a fuel are likely to be addressed by appropriate safeguards and legislation. The manufacturing cost of systems in the power range of 25-150 Watt produced in volumes of over 100,000 units/month has been estimated to be in the range from $1500 to $2500/kW. For systems in the range of 0.1-15 Watts, the costs are not as clear since the relevant miniature systems technologies are still undefined. If the benefits of extended operating hours without recharging can be provided to the consumer, small DMFC portable power

sources are sure to be market competitive with lithium ion batteries even at the current costs projected for larger wattage DMFC applications.

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Figure 6. 50-Watt DMFC system developed by Ball Aerospace and Los Alamos National Laboratory; overall dimensions, 20cm x 20cm x 19cm; output 13.75 V at 3.7 A

Figure 7. 150 Watt DMFC system developed by Giner Electrochemical Systems, Inc.; overall dimension 43 cm x 33 cm x 17 cm; 60 cell stack, 80 cm2 active area, 24 V system output.

Figure 8. Systems developed by Smart Fuel Cell GmbH a. 25 Watt; 12 V; 46.5 cm x24 cm x 16.2 cm; and b. 40 Watt; 12 V; 10 cm x 5 cm x 4 cm.a. 25 Watt and b. 40 Watt systems developed by Smart Fuel Cell GmbH.

Figure 9. Back-to-back multicell stacked configuration schematic and prototype (11 cm x 5 cm x 1 cm, 3 series cells)

Figure 10. 5-Watt Direct Methanol Fuel Cell System with monopolar stack; 4V; 15 cm x 10 cm x 7.5 cm.

Figure 11. 15-Watt system demonstrated by Lynntech Inc. Overall dimensions 27 cm x 12.5 cm x 12.5 cm.

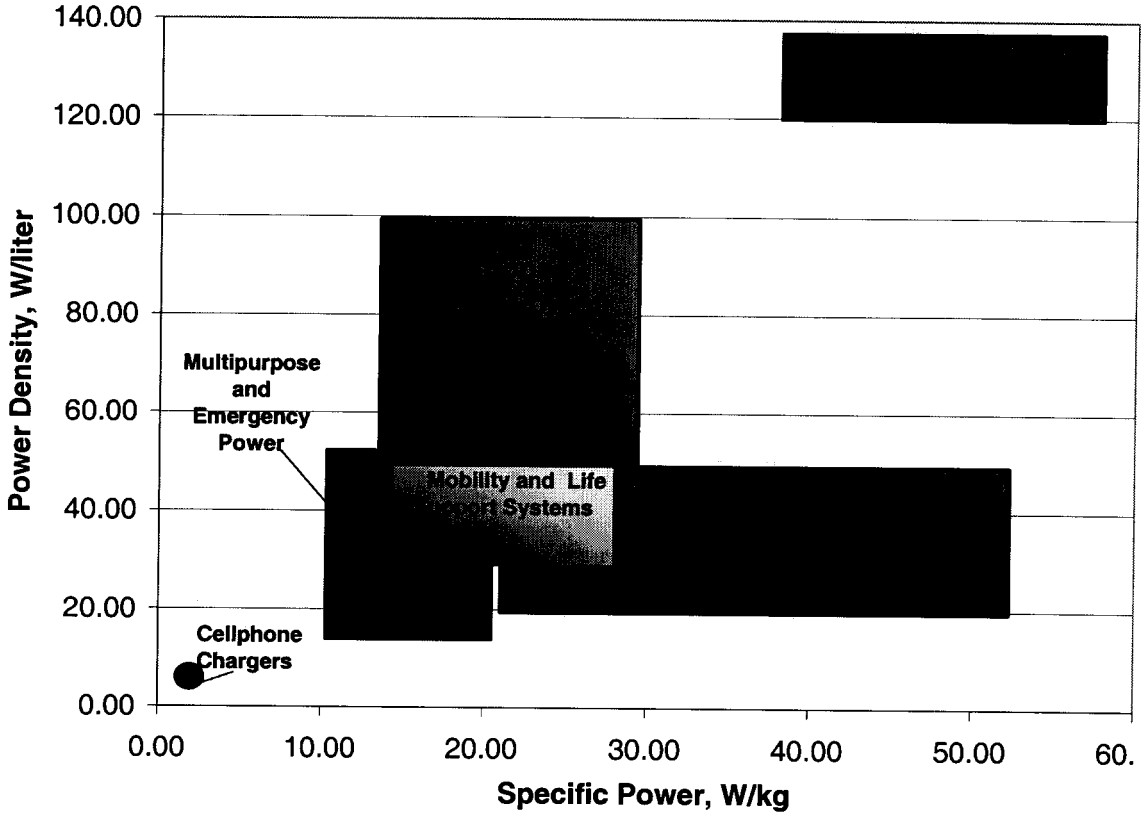
Table 1. Typical Requirements for portable power applications

Application	Power Requirement, Watts	Size, Liter	Mass, kg
Cellular phone battery charger	0.1	0.05	0.1
Portable Phones/Personal Wireless devices	2-5	<0.1	0.1-0.2
Laptop computer, Soldier-Portable Power Source	15-25	<0.4	< 1
Multipurpose Emergency Power Source, Field Battery Chargers	50-100	2-3	< 5
Mobile Rovers	200-400	1.5	< 5
Medical Mobility and life support Back up power	300-500	10	< 10

Table 2. Direct Methanol Fuel Cell Systems in the range of 25-150 Watts

Organization	**System Power,W**	**Weight*,kg**	**Volume, liters**	**W/kg**	**W/liter**	**Reference**
Ball Aerospace	50	6.8	8	7.35	6.3	3
Giner Inc.	150	14	25	10.7	6.0	4
Smartfuel Cell	25	9.7	15	2.5	1.7	5
	40	1.9	2	21.1	20.0	5

*** fuel not included**



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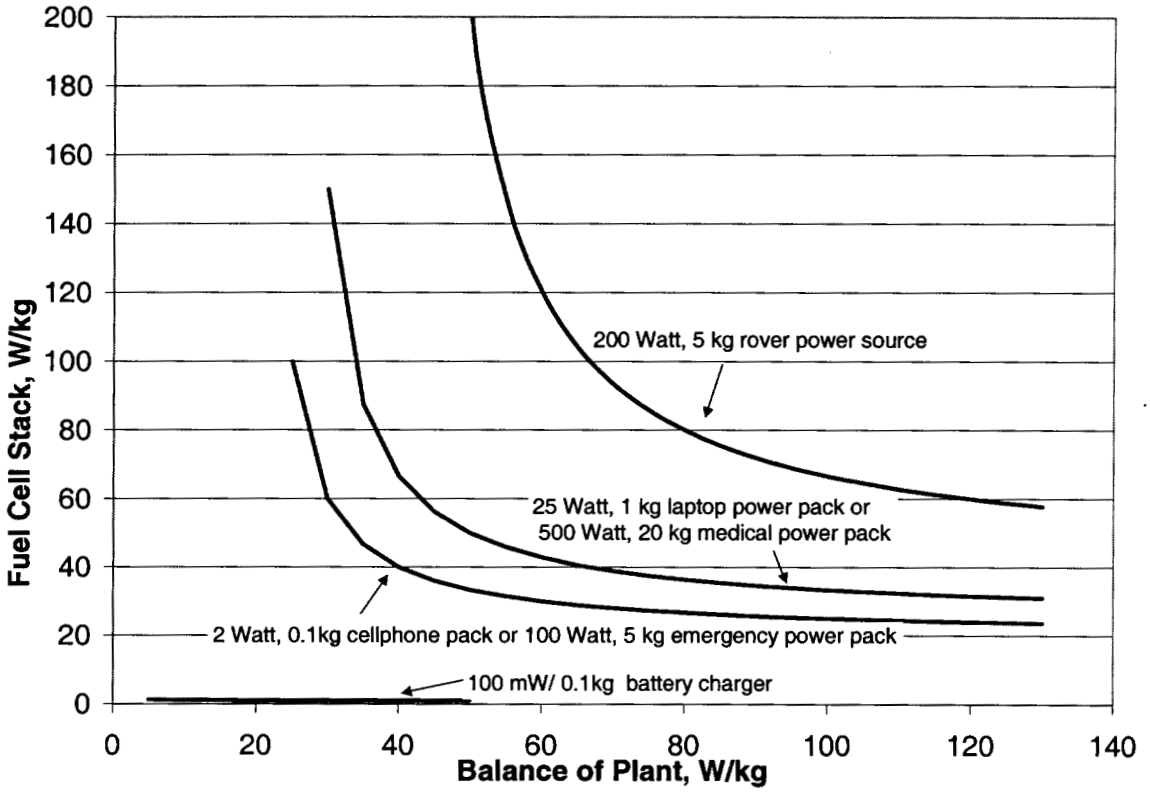
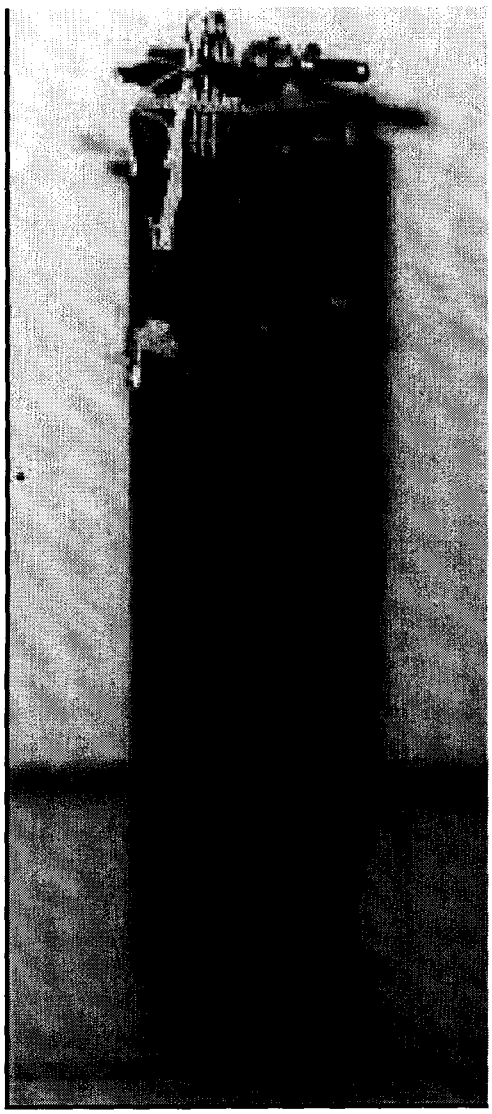


Figure 2. Stack and Balance-of-plant requirements for various applications



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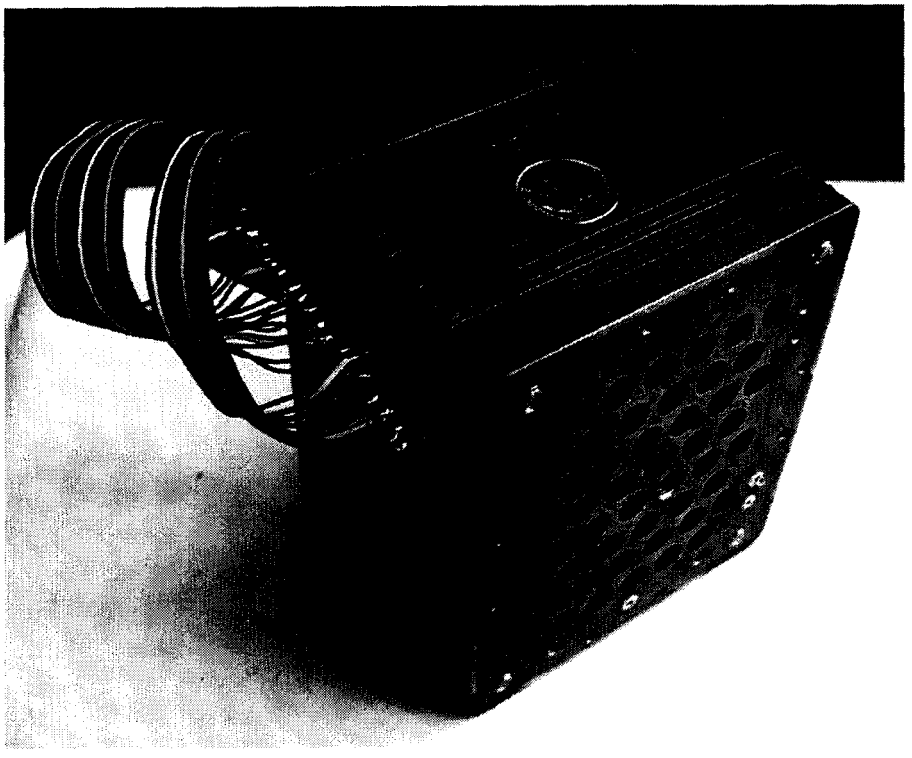

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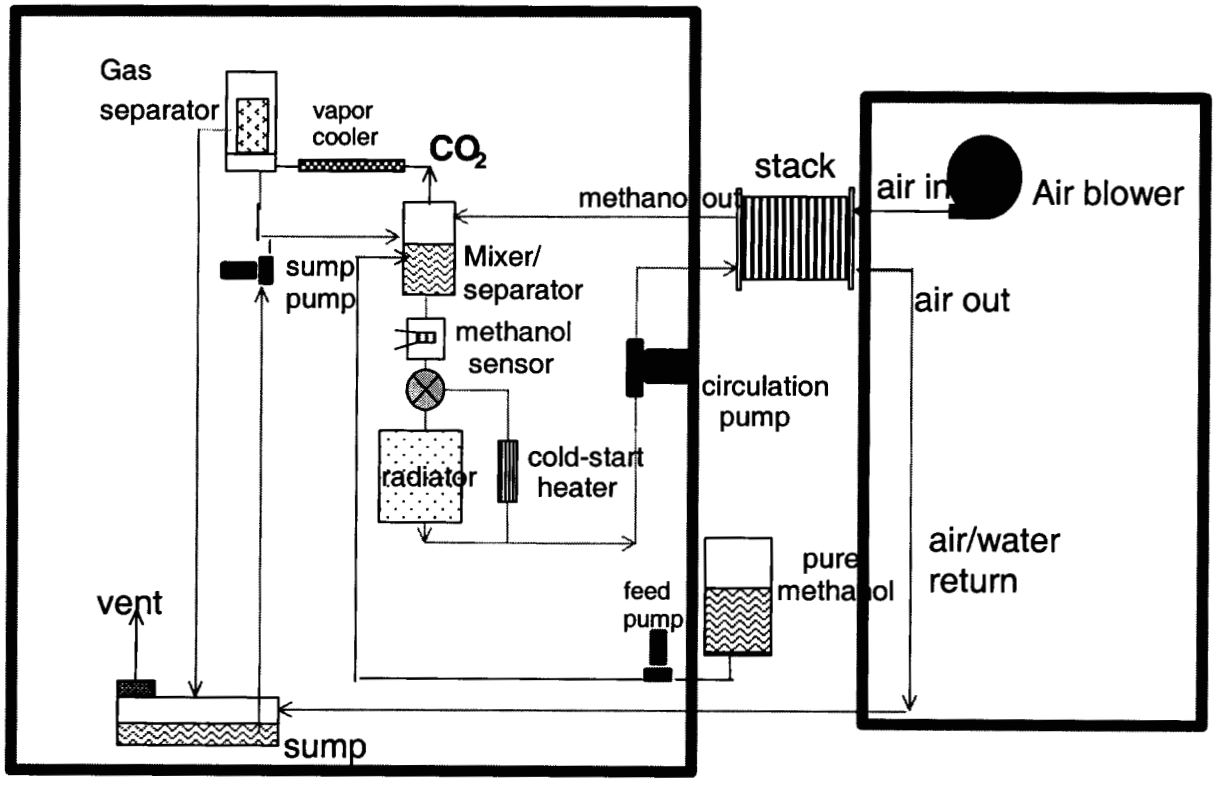

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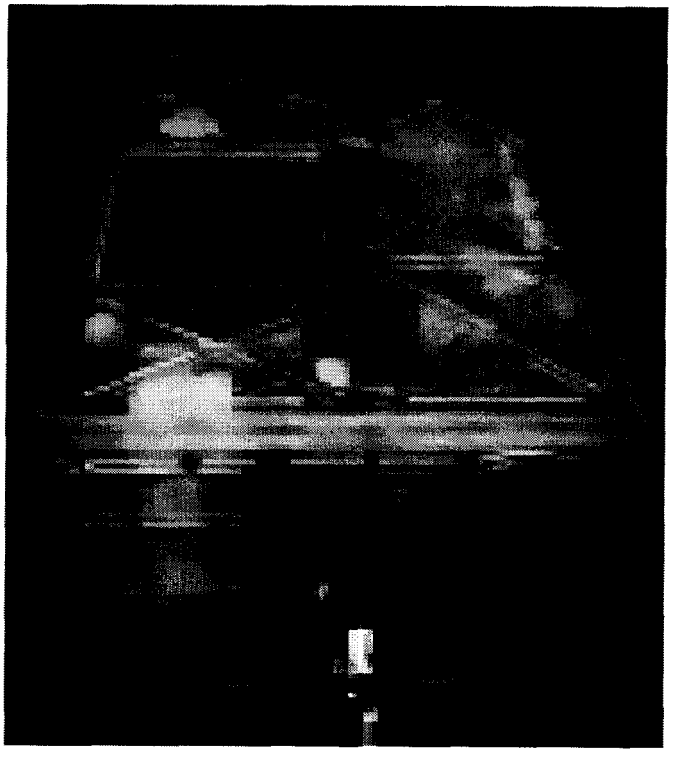

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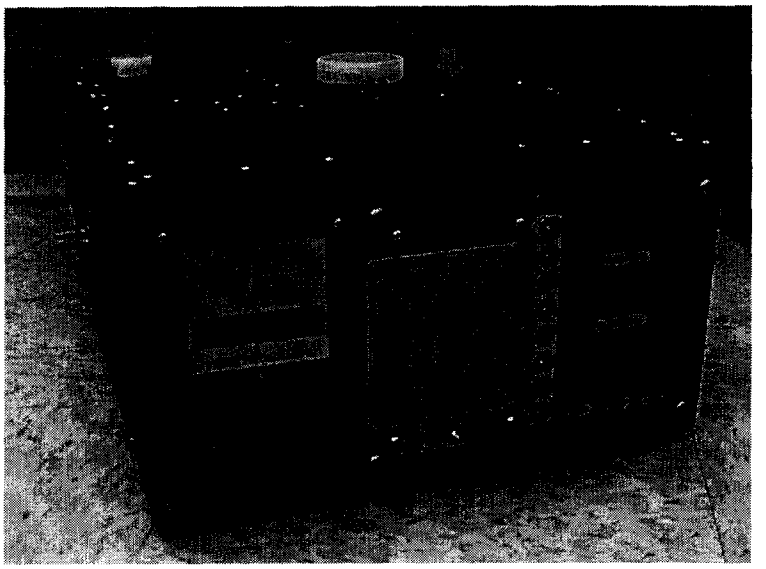

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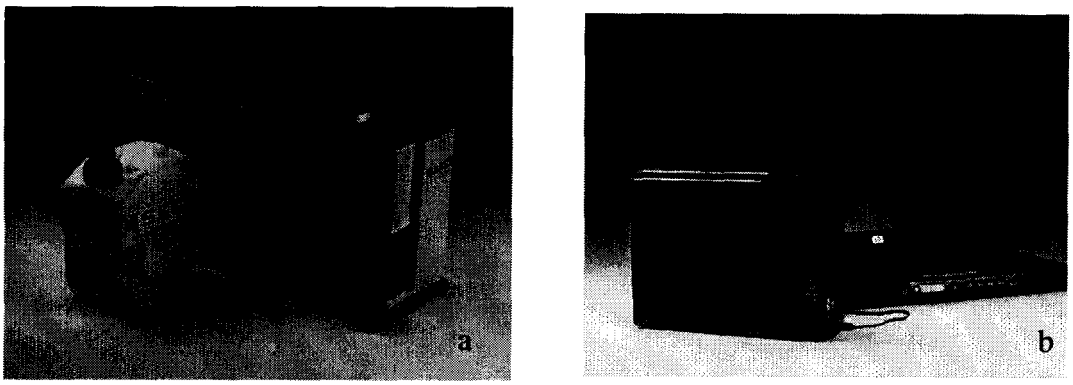

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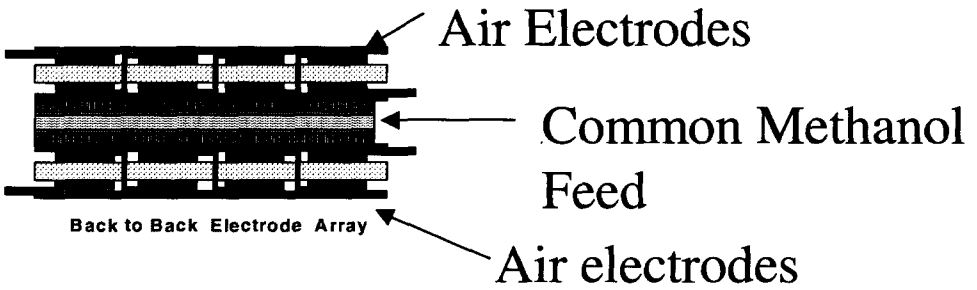

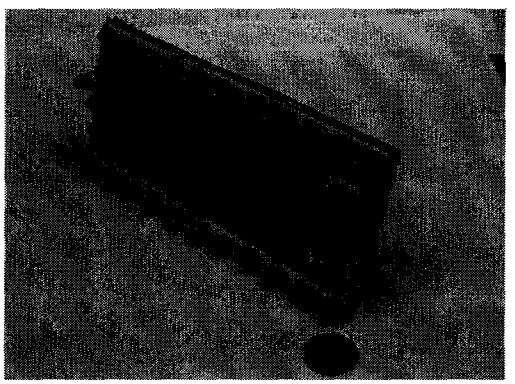

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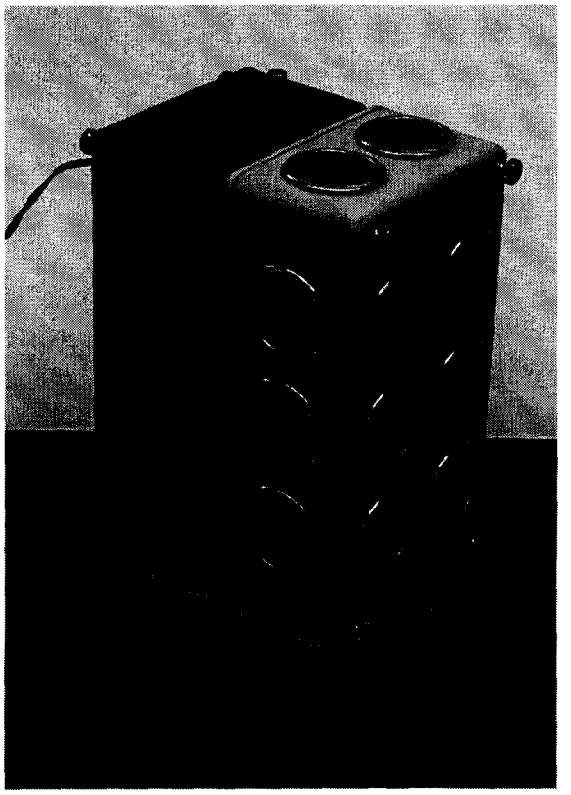

Figure 10. 5-Watt Direct Methanol Fuel Cell System with monopolar stack; 4V; 15 cm x 10 cm x 7.5 cm.

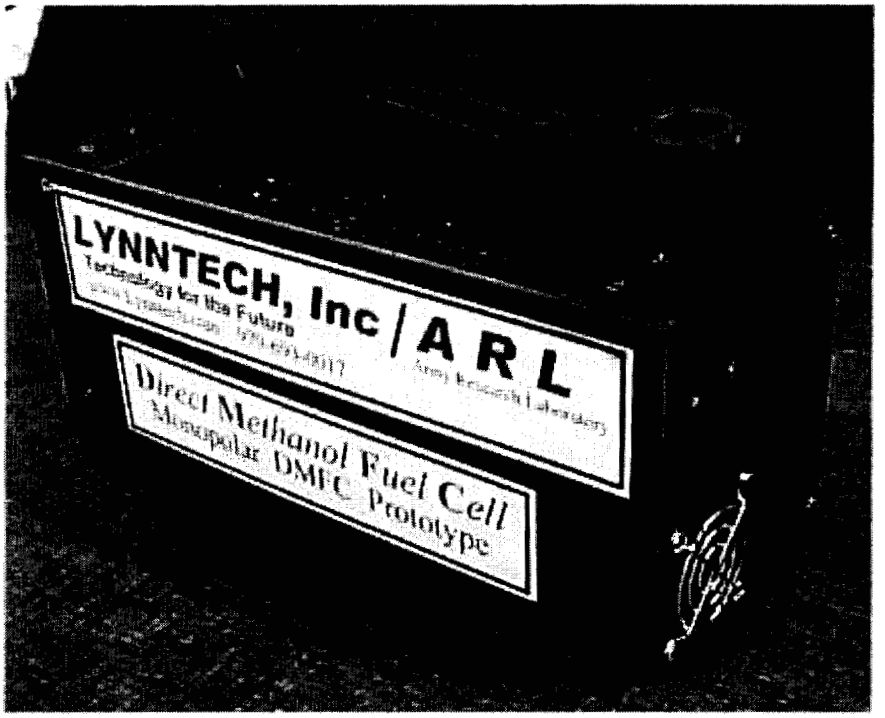

Figure 11. 15-Watt system demonstrated by Lynntech Inc. Overall dimensions 27 cm x 12.5 cm x 12.5 cm.