ELECTROCHEMICAL FACTORS IN DESIGN OF DIRECT METHANOL FUEL CELL SYSTEMS

S. R. Narayanan, T. I. Valdez, N. Rohatgi, J. Christiansen, W. Chun and G. Halpert
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

Abstract

The design of direct methanol fuel cell based portable power source is being pursued at JPL. Performance data obtained on Nafion-based fuel cells have been used to develop a closed loop system model. The model has been exercised to obtain information on the impact of the various possible operating conditions on size, mass and efficiency of portable systems. Flow rate of air, methanol concentration and temperature are found to be key controllable variables that significantly impact system size and efficiency. The results of the modeling studies are discussed.

Background

Recent advances in the performance of direct methanol fuel cells [1-8] are sufficiently attractive for the design of complete power systems. Portable power sources based on this technology are currently being considered for various military applications. The development of a 150 W portable power system based on direct methanol fuel cells is currently being pursued at the Jet Propulsion Laboratory (JPL).

After the initial concept development at JPL over 6 years ago[1], the various factors governing the performance of direct methanol fuel cells have been studied by various groups in the United States and abroad. Performance levels shown in Fig. 1 characterize the status of Nafion-based direct methanol fuel cells being developed at JPL.

![Fig. 1. Performance of a direct methanol fuel cell based on Nafion 117 with Pt-Ru anode and Pt cathode.](image-url)
These fuel cells use in-house developed Pt-Ru catalysts and membrane-electrode assemblies and operate on a liquid feed of aqueous solutions of methanol. While the research in the area of new membranes and catalysts continues, it is important to understand the impact of the current performance levels on the design of systems.

**Brief description of direct methanol fuel cell system**

A portable power system based on the concept of the direct methanol fuel cell is shown in Fig. 2.

![Schematic of a direct methanol fuel cell system for portable applications](image)

Fig. 2. Schematic of a direct methanol fuel cell system for portable applications

In this arrangement the fuel feed subsystem delivers pure methanol into a circulating loop of dilute methanol. Dilute methanol of a specified concentration constitutes the fuel solution entering the fuel cell stack. During operation, the concentration of methanol solution exiting the stack is reduced, and pure methanol must be added to restore the solution to the specified original concentration. Carbon dioxide is rejected from the solution loop at a gas-liquid separator. Air is introduced in the stack with an appropriate device such as a blower or compressor. The exiting air passes through a condenser that serves to recover water and reject heat. A portion of the recovered water may be returned to the fuel circulation loop. Additional heat rejection is accomplished by means of a heat exchanger in the fuel circulation loop. Some of the intrinsic advantages of this arrangement, relative to the hydrogen systems, are that the liquid feed of methanol allows the attainment of a uniform stack temperature and maintenance of membrane humidity.

**Overview of factors affecting system design**

In the design of portable systems based on direct methanol fuel cells the most important performance parameters are: system power density (W/kg, W/L), system energy density (Wh/kg, Wh/L), efficiency (methanol to electricity), performance under transient loads, and long-term stability during operation and storage. Table 1 shows that there are several electrochemical factors that affect system performance.
### Table 1. System Performance Characteristics and Electrochemical factors

| SYSTEM PERFORMANCE CHARACTERISTICS | ELECTROCHEMICAL FACTORS |
|-------------------------------------|-------------------------|
| **Power Density, W/Kg, W/L**        | **Power Density, mW/cm²** (operating point on V-I curve) |
| • Stack Mass                        | • Catalytic activity (Pt-Ru, ...) |
| • Balance of Plant Mass             | • Ionic conductivity (Naion, ...) |
| **Efficiency**                      | • Electrode/MEA characteristics |
| • Stack Heat generation processes   | **Reactant and Product Mass Transfer** |
| • Energy required by pumps and blowers | • Concentration (Methanol Molarity) |
| • Energy required by heat exchangers | • Pressure (Air) |
| • Energy required power conditioning equipment | • Flow rates (Relative to stoichiometric) |
| **Load handling capability**        | • Temperature |
| • Reactant/Product concentration deviations caused by load | • Humidity |
| • Response mechanisms for coping with changes | • Flow field design features |
| **Environment – System sensitivity**| **Water handling through the stack** |
| • Response to temperature, humidity and pressure changes | • Electro-osmotic transport (membrane type) |
| **Operating life**                  | • Temperature of operation |
| • Stable operation for desired periods | **Heat generation processes** |
|                                     | • Irreversibility (Deviation from Thermoneutral potential) |
|                                     | • Crossover Rate (parasitic heat generation) |
|                                     | **Degenerative processes** |
|                                     | • Short term stability (for. e.g. flooding, dry out) |
|                                     | • Long term irreversible loss (catalyst poisoning, membrane degradation) |

Studies at the single cell and stack level have shown that improvements in performance (operating current density and voltage) can be achieved by changing various parameters such as the temperature, concentration and air flow rates and pressures. For example, the data in Fig. 3 shows that considerably higher performance can be attained by operating at high air flow rates. This observation suggests that such an operating mode with enhanced air flow rates will result in improved system performance. Similarly, higher current densities are attainable at higher concentrations of methanol as shown in Fig. 4. This again suggests that higher concentrations of methanol are to be preferred. However, since the system performance, weight and volume are governed by performance characteristics of various subsystems and their interactions with the stack, it is possible that the improvements achieved in stack performance are only ostensible improvements at the system level and may even have a negative impact on the system characteristics. Therefore improvements at the stack level must be assessed in the system context. The
The present study focuses on the identification of the key stack performance factors that are important to achieving a lightweight efficient design for portable applications.

**Fig. 3** Effect of air flow rate on the performance of Nafion-based direct methanol fuel cells

**Fig. 4** Effect of methanol concentration on the performance of Nafion-based fuel cells

**System Modeling**
In order to carry out such an analysis a closed loop steady state system model was developed and exercised. The model sought to relate the inputs and outputs as shown in Fig. 5.

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The model was developed using a set of performance data obtained on a five-cell stack and individual cells fabricated and tested at JPL. Such performance data has been reported earlier [2,5,8]. This data was used to derive multi-variable mathematical correlations to represent the following:

a. Dependence of stack voltage on current density as a function of temperature and air flow rate.

b. Dependence of methanol crossover rate on current density, methanol concentration and temperature.

c. Dependence of water transport rates across the stack on temperature and current density.

In the model the following assumptions have been made. Ambient pressure air flows across the cathodes in the stack. The air exiting the stack is saturated with water vapor. An ambient-air cooled condenser allows recovery of water and rejection of part of the heat generated in the stack. An appropriate portion of the liquid water is returned to the methanol circulation loop and the excess water is rejected. The methanol loop in the process flow diagram consists of a circulating pump, start-up heater for very low temperature start-up (<10°C), and an air-cooled radiator for heat rejection. The carbon dioxide produced in the stack is separated from the liquid stream at a gas-liquid separator. The methanol vapor carried by the exiting carbon dioxide is recovered in an air-cooled condensing unit and returned to the circulation loop.

Upon exercising the model the various sensitivities could be determined. Three controllable variables, namely air flow rate, methanol concentration and stack temperature had the most impact on the system size and efficiency. The results in this regard are discussed in the following.

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Air flow rates and Water Recovery

One of the desirable features of a lightweight system would be not to have to supply or carry water to sustain the operation of the power source. Thus during system operation no more water should be required except for a small initial charge that will be contained in the dilute methanol fuel loop shown in Fig. 2. This would entail restricting water loss from the system to just the amount produced by the reactions. Thus liquid water appearing at the cathode by various processes and the water carried as vapor by the air stream must be largely recovered and returned to the anode side.

Water recovery in small portable systems can be achieved by condensers that use forced ambient air cooling. Under these circumstances, the amount of water recovered is dependent on the ambient temperature, the flow rate of air through the stack, and the heat transfer efficiency of the condenser.

The performance of the single cell and hence the stack is a strong function of the air flow rate as shown in Fig. 3. The stoichiometric air flow rate at any current density is calculated based on the amount of oxygen required for sustaining the electrochemical current producing reaction plus the amount of air consumed by the parasitic oxidation of methanol crossing over to the cathode. The stoichiometric flow rate can be calculated at each value of applied load using the measured value of crossover. An example of this calculation is as follows. A cell operating at 100 mA/cm², with a crossover rate of 40 mA/cm², and an active area of 25 cm², the stoichiometric flow rate of air is about 0.066 liters/min. The air flow in an operating cell can be expressed as a multiple of the stoichiometric rate. Thus a cell operating at 0.33 L/min of air in the above example would correspond to about 5 times the stoichiometric rate. Water recovery parameters can be related to a stoichiometric rate rather than an absolute flow rate.
Fig. 6. Water excess at various stoichiometric rates of air flow (indicated on the lines) at inlet RH=0%, Cathode exit =60°C, 1M methanol, I=100ma/cm², power ~180 W, MeOH Flow rate 2L/min.

The model was exercised to understand the recovery of water at various stoichiometric flow rates and ambient temperatures. These results are shown in Fig. 6.

The results in Fig. 6 show that at stoichiometric flow rates of about 6 or greater, it is not possible to recover enough water at an ambient temperature of about 25°C and there will be a water imbalance. At a lower stoichiometric rate of about 3, water balance can be achieved up to about 37°C. Thus if the fuel cell system has to operate in environments as high as 42°C, the stoichiometric flow rate of 3 will result in a water imbalance condition. Thus the stoichiometric flow rate of air that will allow the maintenance of a water balance is a strong function of the ambient temperature. In order to extend the range of operation to higher ambient temperatures and also ensure water balance, we must operate at stoichiometric flow rates below 3. The condenser duty (heat rejection load) under these conditions is shown in Fig. 7.

The condenser duty increases with stoichiometric flow rate because of the larger amount of water that needs to be recovered. At higher ambient temperatures water cannot be recovered to the same extent as at lower temperatures and the condenser duty decreases. Thus the stoichiometric flow rate has a significant impact on condenser requirements. Metal-based condensers are generally heavy components. Off-the-shelf forced air-cooled condensers are rated at about 200 Wth/kg for such applications. Thus even at a
stoichiometric flow rate of 3 the condenser mass is significant. Condensers need air moving equipment such as fans so that they can maximize their heat transfer efficiency. The power demand by such fans is of the order of 1 Watt-electric for 25 thermal watts. For cooling air to move in and out of the condenser, sufficient volume allowance must be made in the system design. Also, associated with the passage of the cathode stream down the condenser is a pressure drop that adds to the ancillary power demand from the air pumping equipment.

Thus, the need to maintain a water balance and the process of water recovery entails a significant increase in the mass, volume and ancillary power demand. It would therefore be preferable to consider a condition where a condenser need not be used. In order to achieve a water balance without condensing equipment, the model predicts that the stoichiometric flow rates must be as low as 1.75 times the stoichiometric flow rate when the cell is operating at 50-55°C. Under these conditions, the acceptable stoichiometric flow rate becomes a strong function of the operating temperature of the stack. Partial water recovery may be an alternative with minimal impact on mass of the system so that slightly higher flow rates than 1.75 stoichiometric can be used. Therefore performance improvements in the cell at low stoichiometric flow rates is important to achieving a lightweight system.

By operating the stack at temperatures such as 90°C, it is possible to realize higher power densities (see Fig. 1) thus resulting in lower stack mass. However, it is now apparent from this study that operation of the stack temperatures as high as 90°C will necessarily have to involve intensive water recovery, and is not a desirable operating point for realizing a lightweight portable system.

**Methanol concentration and temperature**

The results in Fig. 4 show that by increasing the concentration of methanol, higher power density can be achieved. It is also known that increasing the concentration results in a proportionally higher rate of crossover [2,3,6]. Yet another fact is that the crossover rate in an operating cell decreases as the operating current density is increased [7]. While at higher temperatures the attainable current density is higher, the crossover rate is also strongly increased [1,2,4]. Thus for a particular polymer electrolyte membrane and electrode configuration such as Nafion 117 where the crossover of methanol is a significant process, methanol concentration and temperature strongly impact the overall efficiency of the operating cell. In general, lower cell efficiencies result in a larger heat management system.

The methanol to electric efficiency of the operating cell can be defined as a product of the voltage efficiency and the efficiency of methanol utilization in the current generation process. Such an efficiency product is given by equation (1).

\[
\eta_{\text{stack}} = \left( \frac{V_{\text{load}}}{V_{\text{tn}}} \right) \cdot \left( \frac{I_{\text{load}}}{I_{\text{load}} + I_{\text{cr},1}} \right)
\]

(1)
Where $\eta_{\text{stack}}$ is the efficiency of the operating stack, $V_{\text{tn}}$ is the thermoneutral potential, $V_{\text{load}}$ is the cell voltage under an operating load, $I_{\text{load}}$ is the operating current density and $I_{\text{cr},I}$ is the crossover current density measured at the operating current density. The crossover rate is dependent on current density and this is dependent on electrode and membrane parameters and for the most part can be modelled by a simple linear diffusion model[2]. Introducing such a description of the dependence of crossover rate the efficiency may be expressed as:

$$\eta_{\text{stack}} = \{(V_{\text{load}}/V_{\text{tn}})\} \cdot I_{\text{load}}/\{I_{\text{load}} + \{I_{\text{cr},o} - \gamma I_{\text{load}}\}\} \quad (2)$$

where $I_{\text{cr},o}$ is the crossover rate under open circuit conditions and $\gamma$ is a property of the membrane-electrode assembly and is given by $1/(1 + (D_{\text{el}} \delta_{\text{mem}}/D_{\text{mem}} \delta_{\text{el}}))$, $D_{\text{el}}$ is the apparent diffusion coefficient of methanol in the electrode structure, $D_{\text{mem}}$ the apparent diffusion coefficient of methanol in the membrane, $\delta_{\text{mem}}$ the thickness of the membrane and $\delta_{\text{el}}$ the thickness of the electrode structure[2].

Substituting for $\gamma$ from experimental data into equation (2) and by using appropriate mathematical correlations for the dependence of cell voltage on load, the stack efficiency can be estimated over a wide range of current densities The current density at which the efficiency attains a maximum value can also be calculated. These results are presented in figures 8 and 9.

![Figure 8](image_url)  
**Fig. 8.** Effect of methanol molarity on the current density attained at maximum efficiency.
Fig. 9. Dependence of maximum stack efficiency on molarity of methanol and temperature

These results show that the efficiency of the fuel cell stacks is a strong function of the temperature and concentration. The results also show that current densities as high as 300-500 mA/cm², and efficiency in the range of 25-40%, can be over a wide range of operating conditions.

For lightweight portable systems, high efficiency is a prime requirement. Figs. 8 and 9 show that in order to attain high efficiencies of 40% with Nafion 117 membrane, it is necessary to operate at 60°C and with 0.5 M methanol. The current density values for these operating conditions however would significantly depend on the air flow rates as pointed out earlier here. Experimental data at low stoichiometric flow rates[9] show that the optimal current density under these conditions is in the range 100-120 mA/cm².

Results in Fig. 9 show that the efficiency curve at 60°C decreases with increasing methanol concentration rather steeply. Thus, operating a fuel cell to maintain the maximum efficiency needs close control of methanol concentration and temperature. Maintenance of concentration of methanol requires an in-line concentration sensor that has a response time sufficient to react to the control requirements in a system. Such a sensor has been developed at JPL and has been found to perform satisfactorily in a system configuration.

Conclusions

The key factors governing the size and mass of state-of-art portable systems based on the direct methanol fuel cell concept are air flow rate, methanol concentration and
temperature. By operating at low air flow rates of about 1.75 times stoichiometric, the size of the water recovery system can be minimized or even eliminated. This can be approached by improving the cathode structures to reject water more effectively[9] and by reducing the crossover of methanol through the membrane. The modeling studies suggest that the stack operating temperature of 60°C, appears to be the upper limit for maintaining a thermal and water balance within the size and mass constraints for portable systems. The study also shows that operating systems at a methanol concentration of about 0.5 M allows attainment of high efficiencies with Nafion 117 membranes. Control of concentration is very important in the design of portable systems if high efficiency and thermal balance must be maintained.

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