Latest Version
Correction etc taken care off

Factors Affecting the Design of Direct Methanol Fuel Cell Systems

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

Abstract
Direct methanol fuel cell based power systems are being developed as alternate power sources for portable applications under the sponsorship of DARPA. The paper describes the impact that various processes occurring in the direct methanol fuel cell have on the thermal management, water management, and the overall steady state operation of the power system. Parametric data on electrical performance, fuel crossover, and water transport from operating direct methanol fuel cell stacks has been used to develop a closed-loop system model. This model has been exercised to define overall system design, and to predict the operating strategies that will result in high efficiency, consistent water balance and low system mass. Results of this analysis are discussed.

Background

There has been considerable development of the direct methanol fuel cell (DMFC) technology at the Jet Propulsion Laboratory and at various other institutions under programs sponsored by DOD and DOE in the last seven years. Significant improvements in power density, efficiency, and life have been demonstrated at the cell and stack level in the last few years[1-5]. Today, the liquid-feed direct methanol fuel cell is being actively considered by various energy sectors as a candidate power source for portable applications. The development of integrated power systems based on this concept is now being pursued at JPL under programs sponsored by DARPA and ARO.

The direct methanol fuel cell is based on the electro- oxidation of an aqueous solution of methanol in a polymer electrolyte membrane fuel cell without the use of a fuel processor [1]. The electro-oxidation of methanol occurs on platinum-ruthenium catalyst at the anoded and the reduction of oxygen occurs on platinum catalyst at the cathode. Recent cell performance levels, obtained at JPL, employing air as the oxidant, are shown in Fig. 1. This level of electrical performance is already quite attractive for many applications.

A system schematic of a power system based on DMFC is shown in Fig. 2. 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.

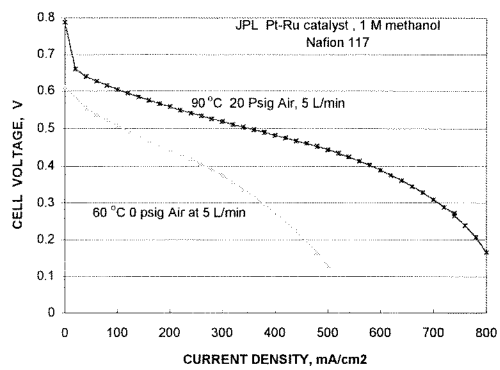

Fig. 1. Performance of DMFC on air at 60°C/0 psig and 90°C /20 psig, and cell active area 25 cm^2.

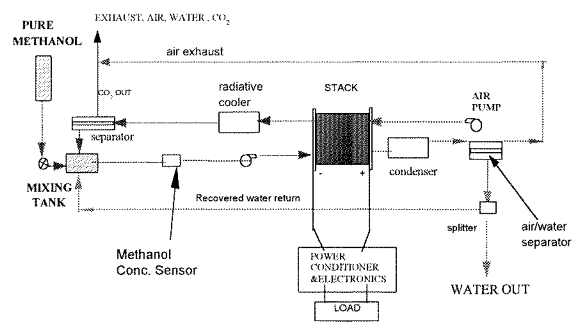

Fig. 2. Schematic of DMFC system.

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 a 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 through a radiator in the fuel circulation loop.

Recent DARPA-sponsored efforts have been directed towards designing a portable power source based on the DMFC system for applications such as battery replacement, battery charging and premium emergency power. In designing such systems it is important to analyze the sensitivities of the overall system and various subsystems to controllable and environmental variables. The following summarizes some of the key results of such analyses for the steady state operation of a 150 W system, and discusses the various factors that are found to be critical to system operation.

System Model Development

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 shown in Fig. 3.

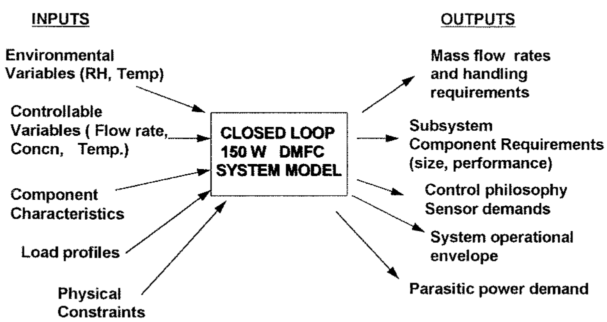

Fig. 3. Input and Outputs relating to exercising the system model

The model was developed using performance data obtained obtained on a five-cell cell stack developed at JPL. This performance data has been reported earlier [5]. Based on this experimnetal data, multi-variable mathematical correlations were developed to represent the following :

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

b. Methanol Crossover rate on current density as a function of methanol concentration and temperature.

c. Water transport rates across the stack as a function of temperature and current density.

The model was also based on the process flow diagram shown in Fig. 4. The various heat and mass management elements of the system are represented in the process flow diagram. 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 operation (<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.

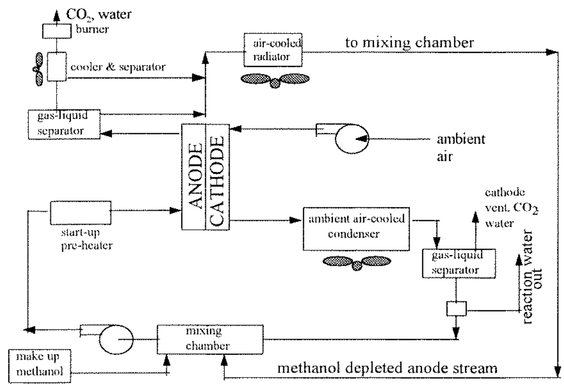

Fig. 4. Process flow diagram for DMFC system model

Results and Discussion

The assumptions were used in exercising the model is described below.

Cathode exit temperature was 60°C and was held constant. Ambient temperature was varied from 25° to 45°C. Air Flow rate was varied from 3 to 6 times stoichiometric. The calculation of the stoichiometric rates included the air demand due to the parasitic process of methanol crossover. Relative humidity was varied from 0% to 100%. Condenser exit temperatures were maintained at 5°C above ambient.,while the exit temperature of the air-cooled radiator was set at 60°C. The operating current density was fixed at 100 mA/cm^2. Methanol concentration in the inlet feed was set at 1.0 M. Cell area was chosen as 80 cm^2, the number of cells was equal to 50, and the gross stack power was about 180 W. The methanol flow rate was set at 40 cc/min/cell. The pressure drop in the anode loop was assumed to be 5 psi and the pressure drop across the cathode was assumed to be 2 psi. The exit temperature of the methanol vapor condenser was set to at 5°C above ambient. No radiation losses were assumed.

Stack power was calculated for the above assumed conditions. Results in Fig. 5 show a strong dependence of stack power on air stoichiometry. The sensitivity of stack power to air stoichiometry can be minimized by enhancing water removal from the backing layers and flow fields. This issue is being addressed by combination of modified electrode structure and modified stack design.

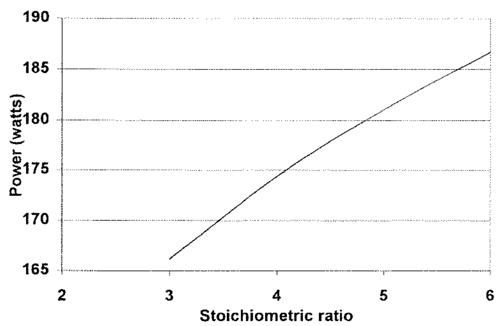

Fig. 5. Calculated Power for 180W (nominal) DMFC stack as a function of air stoichiometry operating at 60°C.

Water balance and thermal balance throughout the system are fundamental requirements for stable system operation. Exercising the model showed that the water balance is a strong function of the ambient temperature and the stoichiometric flow rate of air. The water balance has been analyzed for relative humidity values of 0% and 100% for various stoichiometric rates and ambient temperatures. At the relative humidity of 100% there is always excess water to be rejected over a wide range of temperatures and stoichiometric rates. The amount of excess water amount varies with the stoichiometric flow rate of air and the ambient temperature. However, at a relative humidity of 0%, as typified by a desert environment, the calculations showed important differences in the water balance situation. Under the conditions of 0% humidity, results in Fig. 6 show that at high stoichiometric rates of air flow (for e.g., six times) the water balance can be maintained only below an ambient of 25°C. At lower stoichiometric rates of about 3, the highest operating point is about 37°C.

If stacks can be operated at stoichiometric rates of 3, a rather wide range of temperature operation can be achieved without the loss of water depending on the humidity. However, to ensure water balance at temperatures above 37° C and relative humidity values of 0% , the system design must include a subsystem for water-conservation

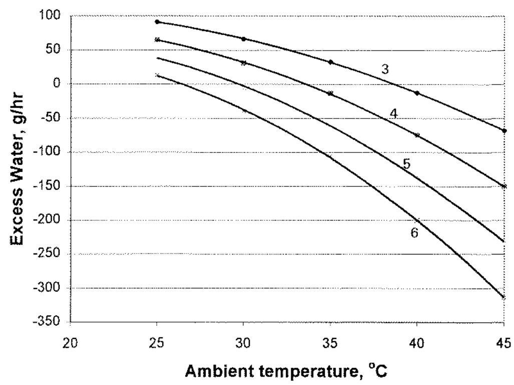

Fig. 6. Excess water at inlet relative humidity = 0%, cathode exit at 60°C. Numbers indicate air stoichiometric rate.

Operation at stoichiometric rates below 3 would be an option if the cell performance does not suffer significantly. With Nafion-based MEAs and present stack designs, operation at stoichiometric rates below 3 presents a significant reduction in cell performance due to water removal problems. However, recent experimental data on MEAs based on alternate membranes, being developed by USC and JPL, have shown that reduced methanol and water permeabilities and high proton conductivity can be realized. This situation presents a prospect of realizing stoichiometric air flow rates lower than 3. Operation at lower stoichiometric flow rates also results in significant reduction in power onsumption for pumping of air even when the pressure drop across the the cathode is only about 2 psi.

The heat rejection systems on the anode and cathode loops operate together to reject about 700 W of heat during system operation. Results in Figs. 7 and 8 show that at low stoichiometric flow rates of air the anode radiator is required to reject about 500 W of heat. Similarly at high stoichiometric air flow rates the cathode condenser duty can be as high as 500 W. With the use of lower stoichiometric air flow rates the system can be made smaller because of the higher efficiency of heat rejection attainable with the liquid-to-air radiator in the anode loop.

The calculations also indicate that operation at temperatures higher than 60°C, for example at 70° or 75° C, will result in a very large heat rejection system because of the high crossover rates exhibited by methanol and the high rates of evaporative water removal at the high stoichiometric air flow rates. From the above analysis, air flow rate is shown to be a critical variable affecting the size and efficiency of DMFC systems

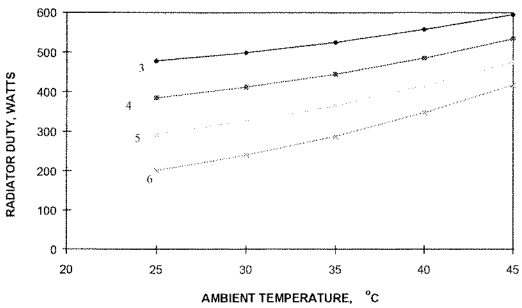

Fig. 7 . Anode radiator duty as a function of air stoichiometry at RH=100%.

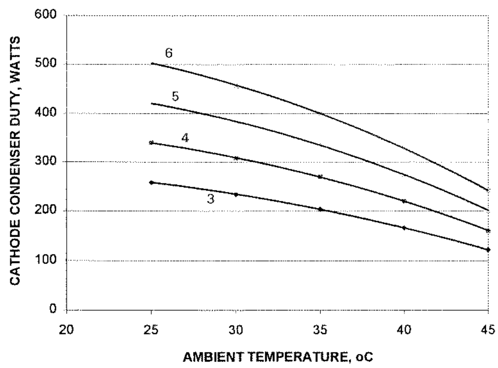

Fig. 8. Condenser Load as a function of air stoichiometry at RH=100%.

Experimental and modeling studies on a 50W system have shown that methanol concentration is also a key parameter governing system size, efficiency and operation. Increases in concentration of methanol by as much as 0.5M results in increased crossover rates, increased heat production, increased air demand, and lower stack performance. Controlling the concentration of methanol is important in achieve steady high performance. Therefore, at JPL we have developed and a fast and robust sensor for monitoring methanol concentration. This has been successfully implemented in the circulating loop (see Fig. 2) . With this sensor the concentration can be controlled and the system output could be maintained at a steady value. Also, methanol crossover can be reduced substantially by using alternate membranes being developed by USC and JPL. The use of these membrane will reduce the sensitivity of the system to small changes in methanol concentration.

The methanol vapor loss at the anode, after condensation of the carbon dioxide stream, ranges from 1-2 g/h for various anode operating conditions. This amount of methanol can be cataytically combusted using the exhaust air from the cathode .

Efforts are currently underway to demonstrate the concepts outlined above in a 150 W power system for DARPA.

Acknowledgment

The work described herein was carried out at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Agency(NASA) and was supported by the Defense Advanced Projects Agency.

References

1. S.Surampudi, S. R. Narayanan, E. Vamos, H. Frank and G.Halpert, A. Laconti, J. Kosek, G. K. Surya Prakash, and G. A. Olah, J. Power Sources, **47** 377 (1994).
2. S. R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M.Smart , S. Surampudi and G. Halpert, Proceedings of the First International Symposium on Proton Conducting Fuel Cells I, p.261-283, The Electrochemical Society, 1995 (Eds. S. Gottesfeld, G. Halpert and A. Landgrebe)
3. S. R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M.Smart, T. I. Valdez , S. Surampudi, J. Kosek and C. Cropley, " Recent Advances in PEM Liquid Feed Direct Methanol Fuel Cells," Proceedings of the Eleventh Annual Battery Conference on Applications an Advances, Long Beach, CA, January 1996.
4. S. R. Narayanan, G. Halpert, W. Chun, B. Jeffries-Nakamura, T. I. Valdez, H. Frank and S.Surampudi, Proceedings of the Power Sources Conference, Cherry Hill, New Jersey, June 1996 .
5 T. I. Valdez, S. R. Narayanan, H. Frank and W. Chun, " Direct Methanol Fuel Cell for Portable Applications," p. 239-244, Proceedings of the Twelfth Annual Battery Conference on Applications an Advances, Long Beach, CA, January 1997.