A Study of the Refractivity Bias in Occultation Retrievals Using End-to-End Simulations

C. O. Ao,[1] T. K. Meehan,[1] G. A. Hajj,[1] A. J. Mannucci,[1] and G. Beyerle[2]

[1] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, USA
[2] GeoForschungsZentrum (GFZ), Potsdam, Germany

It has been shown that the refractivity profiles from GPS/MET have a negative bias with respect to numerical weather prediction models in the lower troposphere. The bias tends to be worse in the moist Tropics, suggesting that sharp refractivity structures arising from water vapor distribution are likely to be a prime causal factor. In this talk, we show that a similar bias exists in the CHAMP and SAC-C data and that the bias depends on the retrieval methods used to process the data. The retrieval methods considered here are the standard (Doppler) method, the backpropagation method, and the canonical transform method. To better understand the underlying causes of the refractivity bias, we employ end-to-end simulations which include full-wave propagation effects on the signal as well as realistic simulation of receiver tracking errors and thermal noise. Our results show that, even under the ideal condition of spherical symmetry and perfect tracking, the current retrieval methods could still result in a negative refractivity bias in the last few kilometers above the surface.

DIRECT METHANOL FUEL CELL SYSTEMS (DMFC): DESIGN FOR PORTABLE APPLICATIONS

S. R. Narayanan* , T. I. Valdez and N. Rohatgi

Jet Propulsion Laboratory

4800 Oak Grove Drive,

Pasadena, CA 91109, USA

*to whom all correspondence is to be addressed

Contact Information:

s.r.narayanan@jpl.nasa.gov

Telephone: (818)354 0013 Fax: (818) 393 6951

Key Word List

Direct Methanol Fuel Cell, Portable fuel cell requirements, system model, water recovery, efficiency, crossover rate, system design, closed loop operation, methanol sensor.

Abstract

Direct Methanol Fuel Cells in portable applications are expected to provide substantially higher energy density and longer operating times over advanced batteries. The time threshold of advantage of using a fuel cell instead of a battery is almost independent of the power level, and is determined by the power density of the fuel cell and its operating efficiency. The various requirements for portable fuel cells that determine system design are defined with examples. The system design process and analysis methods are illustrated. The characteristics of cells and stacks required for system design are described. The dependence of DMFC stack performance on airflow rate, methanol concentration and temperature are necessary for developing closed loop mathematical models for system design. Such a closed loop system model has been developed and the consequences of varying airflow rate on water recovery, thermal management and overall system performance have been analyzed. Using this model, the effect of crossover rate on the overall efficiency, power density and the operating methanol concentrations have also beene investigated. Effect of components on the overall power budget and design issues relating to start-up and transient response are also discussed.

1.0 Introduction: Portable Applications

Portable Applications of fuel cells are generally characterized by a fuel cell power output level of about 1-500 Watts. Fuel cells in such applications are expected to either provide substantially higher energy density and longer operating times over advanced batteries, convenience of instantaneous recharging, and in some cases replacement of small engines to overcome noise and heat signatures. Among the portable applications of fuel cells that are envisaged are military communication systems, portable phones and personal wireless devices that need to be "always on", laptop computers, multipurpose emergency power sources, robotic devices, portable medical devices for life support and mobility, and in general rechargeable battery applications where the operating time exceeds a few hours. The time threshold of advantage of using a fuel cell instead of a battery is almost independent of the power level and can be readily calculated from the efficiency and power density of the fuel cell, and the energy density of the competing battery. Figure 1 is an example of the results from such a calculation. According to these calculations, a 50 W/liter DMFC system operating at a thermal to electric efficiency of 30% can store more energy than a 600 Wh/lit battery if the operating time exceeds 20.5 hours. Such an analysis could be very useful in determining at the outset the energy advantages of DMFC for portable applications.

Figure 1 near here

2.0 Portable System Requirements

Design of systems must be such that the requirements presented by the applications are met. Therefore the first step in the system design is the definition of the requirements. These detailed requirements are classified under the categories of performance, customer interface, weight/volume, environmental tolerance, and safety. The hardware development effort is directed at meeting or exceeding these requirements. Requirements typically include the following characteristics with examples of values :

- System output power : 150 Watts
- Load profile : 300 Watts for 1 sec peak, 150 Watts steady state
- Total operating time: 30 hours before refueling
- Environmental operating conditions (humidity, temperature and chemical composition) : 0°C – 43°C , 0- 100% humidity
- System Mass: 7.5 kg
- System Volume: 10 liters
- System specific power: 20 W/kg
- System power density: 15 W/liter
- Storage temperature: -20°C- 45°C
- Mechanical Shock and Vibration resistance: Must resist 3 foot drop, 500G 10 msec half sine duration
- Orientation insensitivity: must operate within 45 degrees from vertical.
- Safety: spill proof, short circuit protection, etc.
- Emission levels: permissible methanol ...parts per billion in exhaust

- Maintenance : No major maintenance for five years
- Cost : < $2000/kW

It is these requirements determine the stack design, stack operating conditions, materials of construction, design of balance of plant components, and control philosophy.

3.0 System Design Process

The fuel cell power generation system consists of several components that must be integrated and operated as a single unit to deliver the required power. In addition, these components must meet the size, mass and other requirements set forth according to 2.0. Therefore, the system design effort will aim at selecting the best possible system configuration for the specific application and packaging of the entire system within the specified physical envelope.

One of the prime objectives of the system design effort is to define the conditions of stack operation, thermal loads, and mass flows, so that appropriate components can be selected. Basic inputs consisting of the polarization characteristics of a cell or stack, and properties of the reactants and by-products, are integrated into a closed loop system model. Such a model can then be exercised under the constraints determined by the overall system requirements to yield subsystem and control information. Then, the component models and control information for operating heat exchangers, pumps, cooling fans, and sensors, can be combined to select the actual type of component that is appropriate in power

demand and mass/size. These calculations are repeated for a range of stack operating conditions. When mass balance, thermal balance and physical constraints are met, convergence of the model is reached and a system design envelope results. When convergence is not achieved, the result will identify the need for improvement in the components before the constraints are satisfied. Component properties that are part of the system model usually evolve as new technology concepts or new devices are demonstrated. However, the basic thermal and mass flow model is usually unchanged. The importance of such a design exercise is often overlooked during technology development and is delayed until the phase of product development. However, it is recommended that developing even a rudimentary system model would be important in defining realistic goals for focused technology development. Further, the cost and time involved in system development is strongly dependent on the number of hardware trials attempted to meet the performance and packaging requirements. The cost of such hardware development and testing will be significantly reduced by using model predictions and by validating the models using hardware test results. In general, such an iterative and interdependent development of simulation models and actual hardware will minimize the time and cost burden associated with the design, fabrication, testing and successful delivery of the power generation system. The overall flow diagram for the system design process is shown in Figure 2. The system design process and analysis will be illustrated in the following.

Figure 2 near here

4.0 Characteristics of DMFC cells and stacks

The liquid feed 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 [1,2]. The electro-oxidation of methanol to carbon dioxide occurs on platinum-ruthenium catalyst at the anode and the reduction of oxygen to water occurs on platinum catalyst at the cathode. Recent cell performance levels of direct methanol fuel cells realized at the Jet Propulsion Laboratory and in other laboratories suggest that power densities and efficiencies are adequate to be considered for many practical applications. The liquid aqueous feed configuration is important to system design. It allows the polymer electrolyte to be well humidified under a wide range of operating conditions, and allows heat to be removed from the stack effectively. The kinetics of methanol oxidation reaction is a strong function of temperature and therefore the overall power output approximately doubles every 30 degrees in the range 10°C to 90°C. Data at 60° and 90 °C are shown in Figure 3 as examples of this performance characteristic.

Figure 3 near here

At temperatures as high a 90°C, the partial pressure of water vapor is about 0.7 atm and this tends to dilute the oxygen content of the cathode feed stream. Thus, the increase in cathode pressure from 1 atm to 1.5 atm results in substantial improvement in cell performance as shown in Figure 4. However, in portable systems, the use of high pressure is limited as compression of air requires substantial amounts of energy, and raises the power demand by the ancillaries and lowers the overall system efficiency.

Figure 4 near here

The performance of direct methanol fuel cells is also a strong function of airflow rate as shown in Figure 5. This is particularly true at high temperatures and high concentrations of methanol due to methanol crossover placing an excessive demand for air at the cathode. Therefore, results on direct methanol fuel cells at high airflow rates are often reported to show impressive power densities. Increasing the airflow rate entails proportional increase in the rate of evaporation of water from the system resulting in excessive cooling and removal of water beyond what is allowed by the water balance and thermal balance conditions. The use of excessively high flow rates would also involve the use of more energy for air movement. As will be discussed later, airflow rate interacts with several aspects of the system operation and is one of the most critical parameters in the design of portable systems. When methanol concentration is varied the cell power density increases especially when the cell is not limited by air supply at the cathode. This is because increasing the methanol concentration decreases the mass transport limitation at the anode. Results for cells operating on oxygen at 60°C with different concentrations are shown in Figure 6.

Figure 5 near here

Figure 6 near here

However, when air is used instead of oxygen and the airflow rate is limited and not excessive as in the case of the results in Figure 6, the performance sharply declines at methanol concentrations higher than 1M. This is because of methanol permeation

through the polymer electrolyte membrane to the cathode. Methanol that reaches the cathode combines with oxygen and is oxidized to carbon dioxide. Being electrochemically active, methanol lowers the cathode potential and places an extra demand on oxygen that is available for the cathode reaction. The catalytic combustion of methanol and oxygen at the cathode also produces heat. This results in locally higher cathode temperatures and thus higher water vapor pressure which makes mass transfer of oxygen to the cathode electrolyte interface even more difficult. Therefore, methanol crossover places severe restrictions on the operating conditions for the cell, and determines the airflow rate and adds to the heat generation rate. Figure 7 shows the dependence of crossover rate as a function of operating current density for various concentrations of methanol for a Nafion 117-based MEA. The concentration of methanol at the electrode/electrolyte interface decreases as the cell current is increased and this results in a decrease of crossover rate with applied current density. It is important to characterize the crossover rate under open circuit and on load for system design purposes.

Figure 7 near here

The results in Figure 8 show that the crossover rate under open circuit conditions is a strong function of temperature. Another important parameter that needs to be measured is the electro-osmotic transport (drag) coefficient for water in the particular type of MEA. This number is a approximately 2.5-3.0 and connotes that on an average 2.5-3.0 molecules of water are transported by every proton as ionic current flows from anode to cathode. Such data as described above for cells should also be generated for stacks since

some of the parameters such as flow rate of methanol solution and the accumulation of carbon dioxide bubbles in the anode compartment resulting from the specific flow field design could be influence the polarization behavior [3-5].

Figure 8 near here

Data in Figures 3-8 can be used to derive basic multi-variable mathematical correlations to represent the following :

- Dependence of stack voltage on current density as a function of temperature and airflow rate.
- Dependence of methanol crossover rate on current density, methanol concentration and temperature.
- Dependence of water transport rates across the stack on temperature and current density.

Results at the single cell and stack level show that improvements in performance (operating current density and voltage) can be achieved by changing various parameters such as the temperature, concentration and airflow rates and pressures. 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 the next step of the effort in system design process of exercising the model for

specific system constraints allows us to assess these improvements at the stack level in the system context.

5.0 System Configuration and Model Assumptions

A portable power system based on the concept of the direct methanol fuel cell is shown in Figure 9.

Figure 9 near here

In this system configuration 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 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 as and when needed. Additional heat rejection (usually a major portion of the thermal load) is accomplished by means of a heat exchanger in the fuel circulation loop. Some of the intrinsic advantages of this configuration, relative to the hydrogen systems, are that the liquid feed of methanol allows the attainment of a uniform stack temperature and the maintenance of

membrane water content at all times. As per the flow chart in Figure 2, this type of configuration definition is a pre-requisite to the development of a system model.

In the development of a system model the following assumptions have been made with respect to the system configuration. 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. Some of the methanol vapor carried by the exiting carbon dioxide is recovered in an air-cooled condensing unit and returned to the circulation loop and the remaining traces of methanol vapor are combusted catalytically after combining the carbon dioxide exhaust with the air exhaust.

Exercising the system model and achieving convergence will result in the development of a thermal and mass flow diagram of the kind shown in Figure 10 . Upon exercising the model various sensitivities can be determined. The basic constraints shown are power output at the stack level, pressure drops, ambient temperature and humidity. These constraints are needed to carry out the exercise of steady state modeling. Results of modeling show that for a 150-Watt system required to operate under an ambient of 42°C and 0% relative humidity, three controllable variables, namely, airflow rate, methanol

concentration and stack temperature have the most impact on the system size and efficiency. These results are discussed in the following.

Figure 10 near here

6.0 Airflow rates and Water Recovery

One of the desirable features of a light-weight system would be not to have to supply water to sustain the continuous 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 Figure 9. This would entail restricting water loss from the system to just the amount produced by the reactions. Therefore, the water carried as vapor by the air stream and the water transported by electro-osmotic processes 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 airflow rate as shown in Figure 5. The stoichiometric airflow rate at any current density is calculated from 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 values of methanol crossover rate. An example of this calculation is as follows. For a cell operating at 100 mA/cm^2, with a crossover rate of 40 mA/cm^2, and an active area of 25 cm^2, the stoichiometric flow rate of air is about 0.066 liters/min. The airflow 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.

The model was exercised to understand the recovery of water at various stoichiometric flow rates and ambient temperatures. The results in Figure 11 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 under the operating conditions for the stack, and there will be a water imbalance. At a lower stoichiometric rate of about 3, water balance can be achieved up to an ambient temperature of 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 again result in a water imbalance condition. The stoichiometric flow rate of air that will allow the maintenance of a water balance is thus 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 or higher pressures than ambient pressures. These results are a strong function of the stack operating temperature, since the exit stream from the cathode side of the stack is assumed to be saturated with water at the stack temperature. Operating at lower stack temperatures will

allow for a wider range of environmental operating temperatures and airflow rates. However, the penalty of operating at lower temperatures is a larger stack. By operating the stack at temperatures such as 90°C, it is possible to realize higher power densities (see Fig. 3) thus resulting in lower stack mass. However, it is now apparent from exercising the model 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. Therefore, the physical constraints such as the overall mass and size will determine the stack operating temperature. If we choose to operate at 60°C, the condenser duty (heat rejection load) under these conditions is shown in figure 12.

Figure 11 near here

Figure 12 near here

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 W_{th}/kg . 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 1Watt-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 flow from the exit of the cathode through the condenser is a pressure drop that impacts power demand by the air supply 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. This is particularly a limitation for portable fuel cells where weight and volume are premium. 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. Consequently, performance improvements in the cell at low stoichiometric flow rates is important to achieving a lightweight system. More recently, JPL has been able to develop fuel cells which can operate at low stoichiometric airflow rates and the performance is shown in Figure 13.

Figure 13 near here

With these membrane electrode assemblies, a 150-Watt DMFC system that does not require a condenser is expected to weight no more than 8 kg.

7.0 Power Density and Efficiency

The results in Figure 6 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 (Figure 7). Also from Figure 7 it is clear that the crossover rate in an operating cell decreases as the operating current density is increased [6]. While higher temperatures allow the attainment of higher current density, the crossover rate also increases[1,3,7]. For a particular polymer electrolyte membrane and electrode configuration with Nafion 117, where the crossover of methanol is significant, 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. There have been efforts to develop new membranes with low crossover. In particular, the efforts of the University of Southern California and the Jet Propulsion Laboratory on the development of interpenetrating networks of polystyrenesulfonic acid- PVDF membranes have shown about 75% reduction in crossover relative to Nafion [8]. These membranes have successfully been demonstrated in stacks with an active electrode area of 80 cm^2. Short-term testing over a few days has not shown any evidence of degradation. Other recent efforts to reduce crossover that have been successful include those from DuPont and Samsung[9,10]. The impact of methanol crossover on efficiency and power density for the system will now be discussed in the following.

7.1 Influence of methanol Crossover

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).

$$\eta_{stack} = (V_{load}/V_{tn}) \cdot (I_{load}/(I_{load} + I_{cr,I}) \quad (1)$$

where η_{stack} is the efficiency of the operating stack, V_{tn} is the thermoneutral potential, V_{load} is the cell voltage under an operating load, I_{load} is the operating current density and $I_{cr,I}$ is the crossover current density measured at the operating current density.

The crossover rate is dependent on current density and this is in turn is dependent on electrode and membrane parameters. These dependences for the most part can be modeled by a simple linear diffusion model [3]. Introducing such a description of the dependence of crossover rate the efficiency may be expressed as:

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

where $I_{cr,o}$ is the crossover rate under open circuit conditions and γ is a property of the membrane-electrode assembly (MEA) and is given by $1/\{1+ (D_{el}\,\delta_{mem}/D_{mem}\,\delta_{el})\}$, D_{el} is the apparent diffusion coefficient of methanol in the electrode structure, D_{mem} the apparent diffusion coefficient of methanol in the membrane ,δ_{mem} the thickness of the membrane and δ_{el} the thickness of the electrode structure [3].

Substituting for γ 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 14 and 15. According to these results the efficiency of the fuel cell stacks is a strong function of the temperature and methanol concentration. The results also show that current densities as high as 300- 500 mA/cm^2 , and efficiency in the range of 25-40% , can be attained over a wide range of operating conditions.

Figure 14 near here

Figure 15 near here

For lightweight portable systems, high efficiency is a prime requirement. Figure 14 and 15 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 airflow rates as pointed out earlier here. Experimental data at low stoichiometric flow rates [11] show that the optimal current density under these conditions is in the range 100-120 mA/cm^2.

Results in Figure 15 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. This type of sensor is also quite amenable to miniaturization for portable systems [12].

7.2 Best operating conditions

In summary, the key factors governing the size and mass of state-of-art portable systems based on the direct methanol fuel cell concept are airflow rate, methanol concentration and temperature. By operating at low airflow rates of about 1.75 times stoichiometric, the size of the water recovery system can be minimized or even eliminated. This can be achieved by improving the cathode structures 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. 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. Membranes with lower crossover rate will allow us to operate at even lower airflow rates and also higher methanol concentration. The higher the methanol concentration that can be sustained in the anode loop, the greater is the transient power capability and the ability to extend the fuel cell operating range for applications with a widely varying load profiles.

8.0 Components and Power Budget

Component models for pumps, gas-liquid separators, fans and sensors will have to be integrated with the thermal and mass flow model to identify components that satisfy the constraints of overall system weight and volume. Usually condensing equipment is heavy and it would be preferable not have to recover any water. Choosing the system operating parameters to ensure minimal water recovery would significantly reduce the weight in the system. Minimizing the number of cooling stages will also minimize power losses. Choosing a stack design with minimal pressure drop is key to designing an efficient system. Beyond the pressure drop of a few centimeters of water, even low levels of compression can be power demanding because of the low efficiency of pumping air. Using a blower and avoiding a condenser the power budget for the balance of power components power budget inclusive of control electronics for a 150-Watt DMFC system is about 38 Watts. Further, DC/DC-conversion to provide a regulated output can entail as much as 20 Watts, even with highly efficient converters. The losses in the latter step may be avoided as terminal equipment such a chargers and other portable electronics are usually equipped with a dc voltage conditioning stage within the device that can tolerate a wide voltage input swing. Where weight constraints are significant, such as in ultra-portable systems for consumer electronics, lightweight stack designs based on mono-polar configurations [13], airflow under natural convection and elimination of condensing equipment must be implemented. Monopolar stack configurations offer a three-fold increase in power densities over conventional bipolar designs at power levels up to 25 Watts. However designs based on air supplied by

natural convection do not provide adequate air-moving resources to handle liquid water that appears on the cathode and thus could render the stack orientation sensitive.

Gas liquid separation from the system is readily accomplished using microporous membranes that are impermeable to solutions while permeable to gaseous carbon dioxide. However, venting of by-products from the DMFC system must be carefully controlled in a consumer environment due to the toxicity of methanol. Water vapor release into a confined environment could result in local saturation and condensation of liquid water. The rate of carbon dioxide emission from a DMFC system operating at 20 Watt system approximately equals that generated by a human being. Sequestering the carbon dioxide is not a weight-effective proposition. Any release of methanol vapor from the system must also be avoided. The carbon dioxide exhaust should be passed through a clean-up stage using catalytic oxidation devices so that any trace of methanol vapor is completely converted to carbon dioxide before release.

9.0 Start-up and transient response

Start-up functions for the DMFC system will be supported by a rechargeable battery, and the battery power will be utilized only until the reactants are made available to the stack. Since the DMFC stack is capable of significant power output at low temperatures, system resources can be readily supported by the stack even at an ambient temperature of 15°C. The heat generated by the stack can then be used to raise the internal temperatures. During the heat-up period which could be up to five minutes depending on the heat generation scheme, the battery can also serve as a source of additional power

wherever the weight constraints permit a larger battery. In systems where the power must be available at all times, the fuel cell should be left in the "on" state at a low standby power level so that the heat generation can be taken advantage of to maintain the internal operating temperatures. Where power swings are significant with frequent start-up and shut-down cycles and full rated power is needed from the moment of start-up, a truly hybrid configuration with a rechargeable battery will eliminate the transient response requirements on the fuel cell, maximize efficiency, and reduce the complexity of controls. The rechargeable battery will be kept charged at all times by using a small fraction of the power from the operating fuel cell.

10 Summary and outlook

More recently integrated DMFC systems have been designed and demonstrated by various organizations such as the Jet Propulsion Laboratory, Ball Aerospace Corporation, Giner Inc., and Smart Fuel Cell Inc., using the principles described herein. Such systems have demonstrated overall system efficiencies that range from 20%-30% and power densities of about 10-15 W/L. Continuous operation with pure methanol feed taking advantage of methods for methanol concentration control has been demonstrated. Partial water recovery has allowed system operation to be extended to 45 °C and 0% relative humidity. The system power densities that have been demonstrated are rather low, although none of the demonstrations were specifically directed towards weight or volume optimization. In the future, the interest in small direct methanol fuel cell systems is likely to grow as weight and volume reductions demanded by portable electronic device applications are addressed. Early market entry for portable direct methanol fuel cells is

expected to be in applications that are the least demanding from the consumer perspective such asmulti-purpose auxiliary power sources that function during emergencies or in remote areas. Early DMFC systems are likely to be deployed in a hybrid configuration with rechargeable batteries so that power density and start up issues can be readily addressed.

Acknowledgement

The work presented in here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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. US Patent No. 599,638 "Aqueous liquid feed organic fuel cell using solid polymer electrolyte membrane"
3. 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)

4. 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.
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.
6. S. R. Narayanan, T. Valdez, N. Rohatgii, J. Christiansen, W.Chun, G. Voecks and G. Halpert, Proceedings of the Power Sources Conference, Cherry Hill NJ, June 1998.
7. X. Ren, T. A. Zawodinski, F. Uribe, H. Dai and S. Gottesfeld, in Proton Conducting Fuel Cells I, S. Gottesfeld, G. Halpert and A. Landgrebe, Editors, Electrochemical Society, Pennington, NJ, (1995) p. 284.
8. G. K. Surya Prakash, M. Smart, A.R.Atti, G.A. Olah, S.R. Narayanan, T.Valdez and S.Surampudi, " Low Crossover Polymer Electrolyte Membranes for Direct Methanol Fuel Cells", Abstract 406, Electrochemical Society Meeting, October 1999, Honolulu, HI.
9. Raj Rajendran, "Progress in Membrane Development for DMFC Technology" presented at the Small Fuel Cells Conference, Washington DC April 2002, Organized by Knowledge Foundation Inc.

10. H. Kim, C.Lim and H.Chang, "Fabrication and Direct Methanol Fuel Cell Applications of Nafion based Organic-Inorganic Hybrid Membrane" Proceedings of the International Symposium on Direct Methanol Fuel Cell Symposium, Electrochemical Society Inc., Volume 2001-4, p. 14-28.

11. T. I. Valdez and S. R. Narayanan, "Recent Studies on Methanol Crossover in Liquid-Feed Direct Methanol Fuel Cells" Proceedings of Symposium on Proton Conducting Fuel Cell 2, Electrochemical Society, Volume 98-27, p. 380-387.

12. S. R. Narayanan, T. I. Valdez and W. Chun, Electrochemical and Solid State Letters, **3** (2000) 117-120.

13. S. R. Narayanan, F. Clara and T. I. Valdez, "Development of Miniature Fuel Cell for Portable Applications", Proceedings of the International Symposium on Direct Methanol Fuel Cell Symposium, Electrochemical Society Inc., Volume 2001-4, p.254-264.

List of Figures

Figure 1. Time threshold of advantage of direct methanol fuel cell systems over a specific battery system.

Figure 2. Flow Diagram depicting the Process of System Design

Figure 3. Effect of temperature on the performance of liquid feed DMFC.

Figure 4. Effect of pressure on the performance of DMFC

Figure 5. Effect of varying airflow rates on DMFC performance.

Figure 6. Effect of methanol concentration on DMFC that is not cathode limited.

Figure 7. Dependence of methanol crossover rate on current density for a Nafion 117 MEA.

Figure 8. Dependence of methanol crossover rate on concentration of methanol and cell temperature.

Figure 9. Schematic of a direct methanol fuel cell system for portable applications

Figure 10. Thermal and Mass flow diagram that is obtained as a modeling exercise

Figure 11. Water excess at various stoichiometric rates of airflow (indicated on the lines) at inlet (1 atm, RH=0%, Cathode exit = 60°C, 1M methanol, I = 100 mA/cm^2, power ~180 Watts, MeOH Flow rate 2L/min)

Figure 12. Condenser duty as a function of stoichiometric flow rate (RH=0%, Cathode exit = 60°C, 1M methanol, I = 100 mA/cm^2, power ~180 W, MeOH Flow rate = 2L/min)

Figure 13. Performance of Nafion 117 MEA with improved cathode structure; electrode area 25 cm^2.

Figure 14. Effect of methanol molarity on the current density attained at maximum efficiency

Figure 15. Dependence of maximum stack efficiency on molarity of methanol and temperature

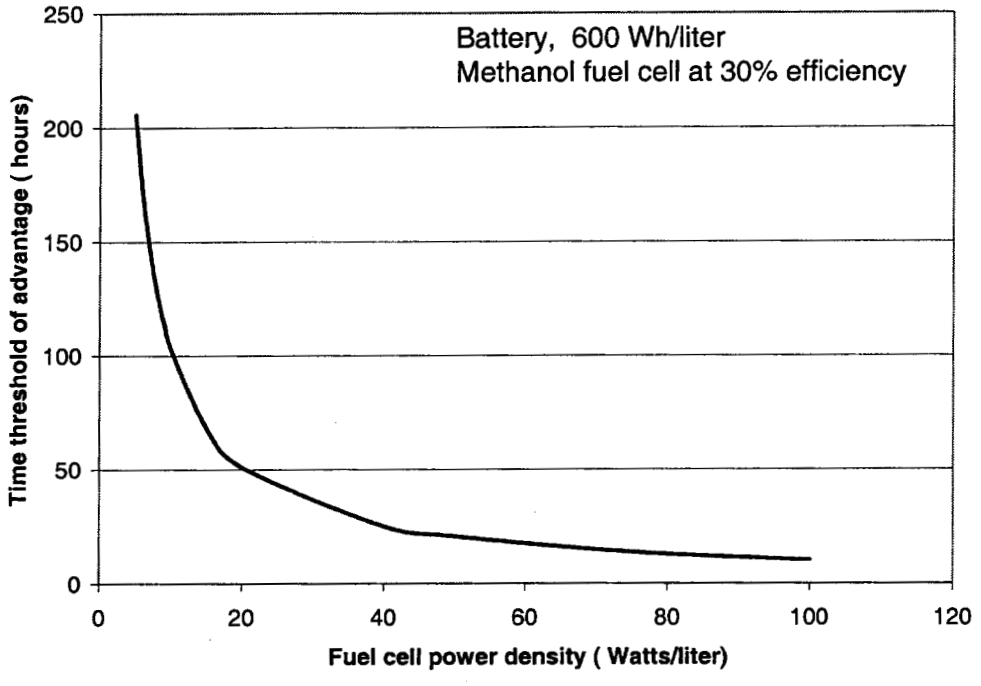

Figure 1. Time threshold of advantage of direct methanol fuel cell systems over a specific battery system.

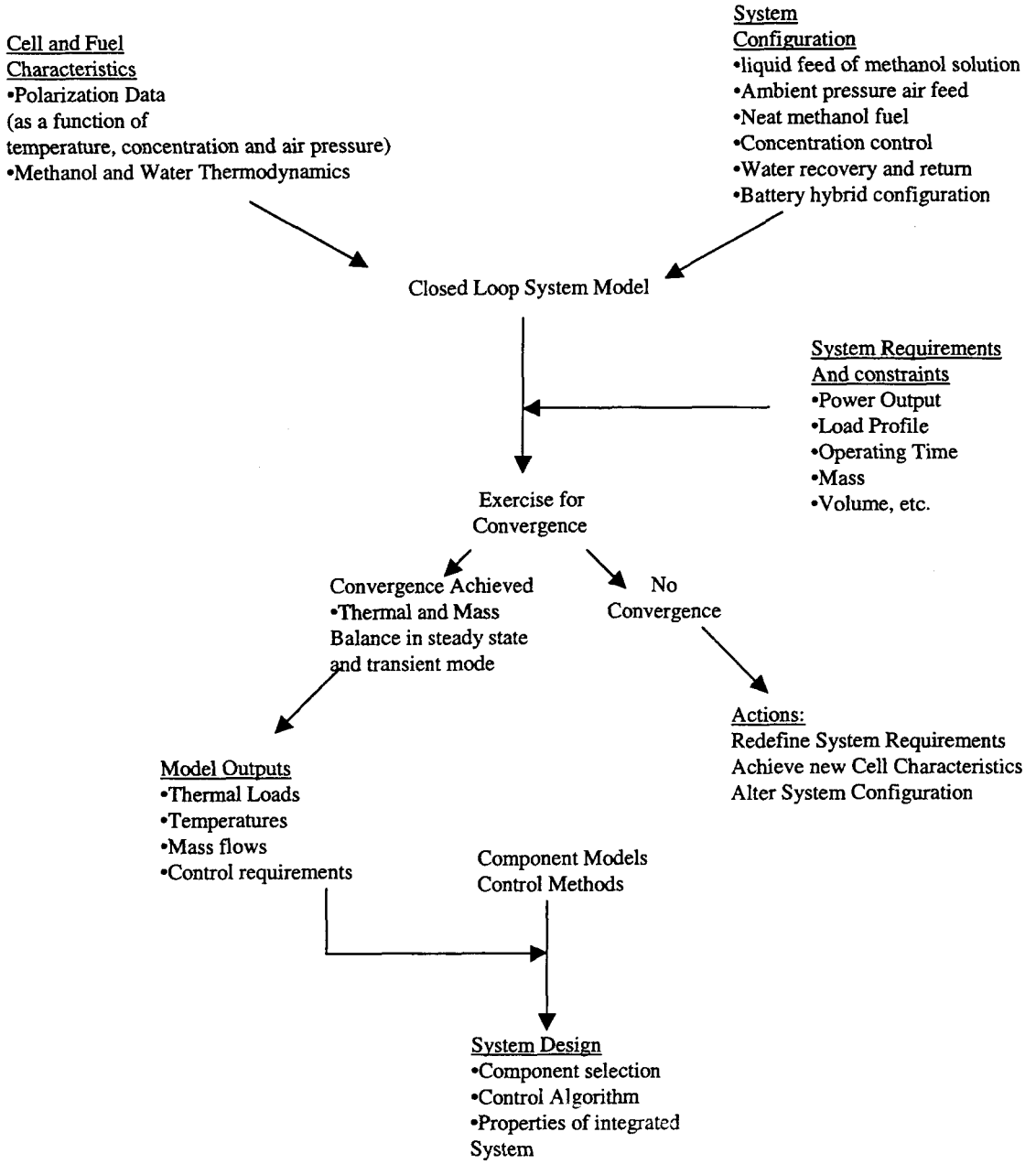

Figure 2. Flow Diagram depicting the Process of System Design.

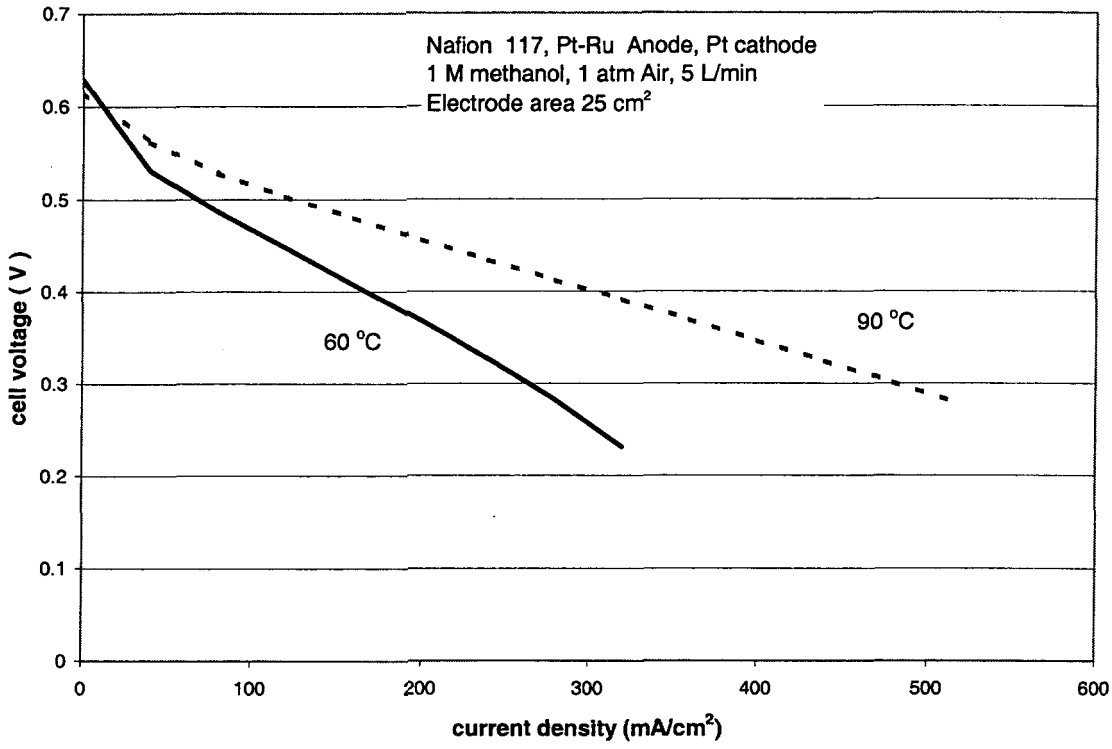

Figure 3. Effect of temperature on the performance of liquid feed DMFC.

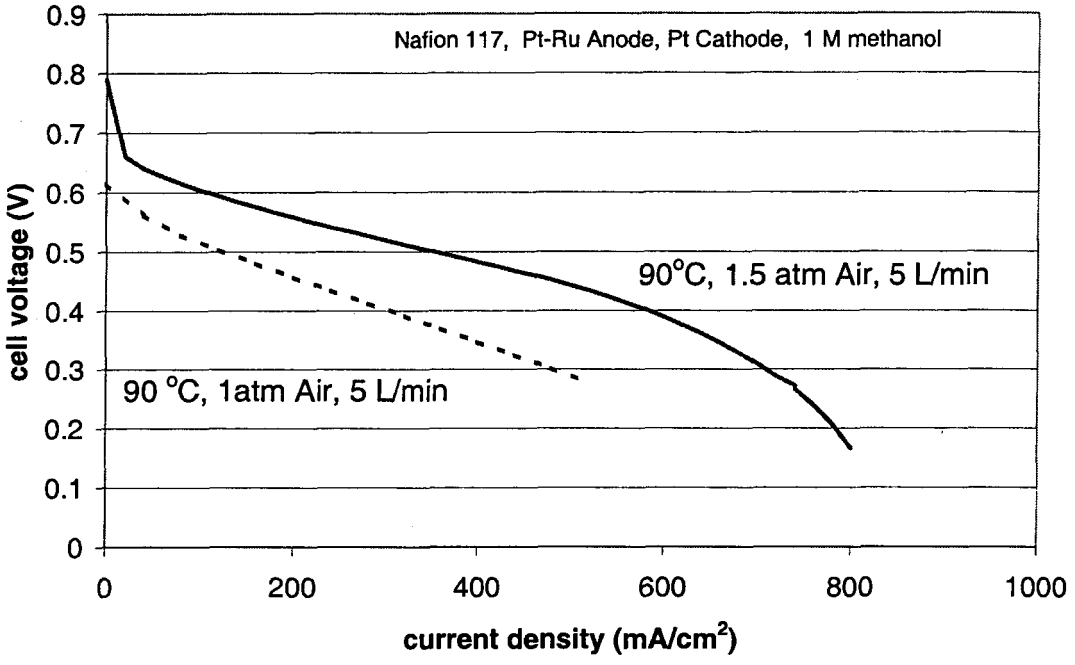

Figure 4. Effect of pressure on the performance of DMFC

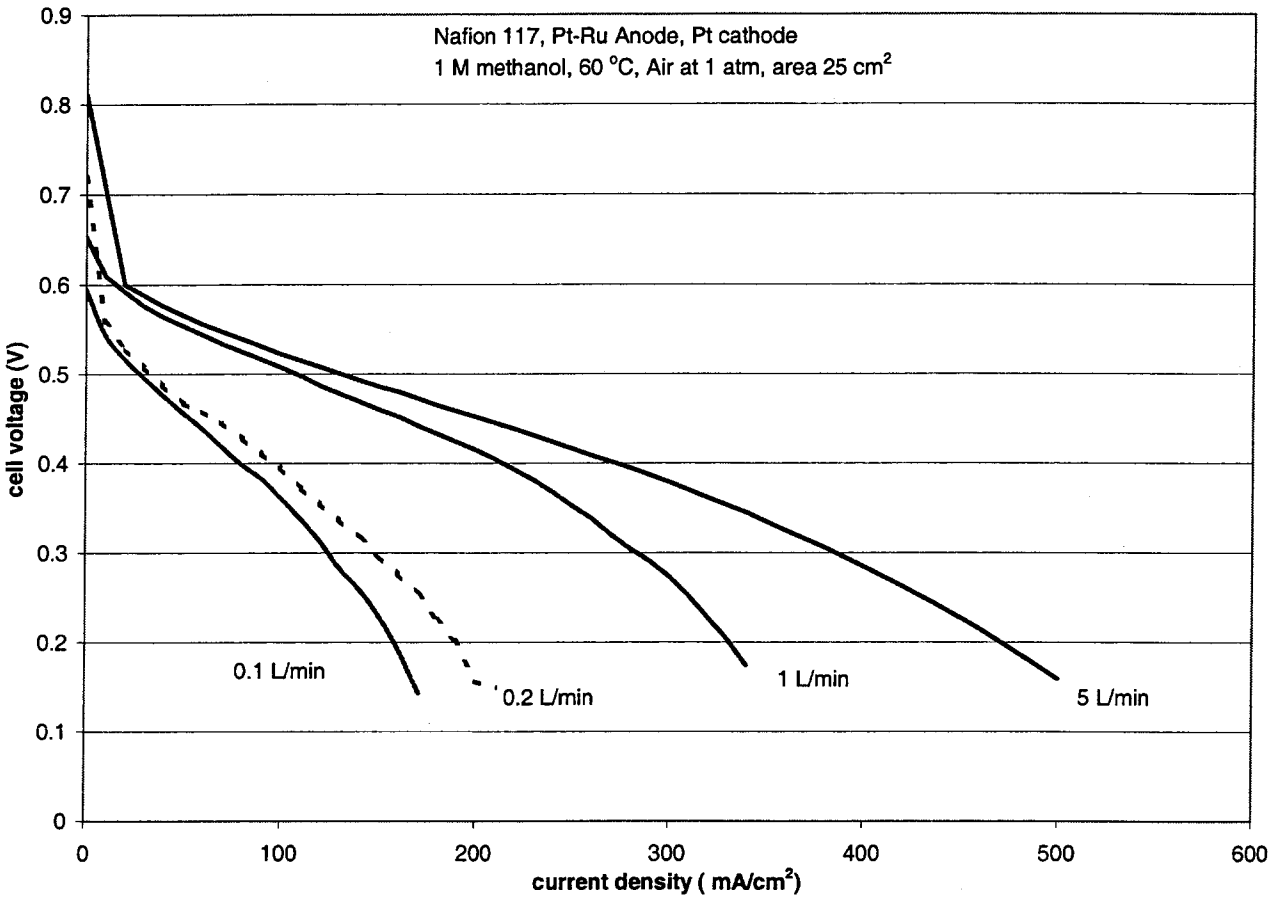

Figure 5. Effect of varying airflow rates on DMFC performance.

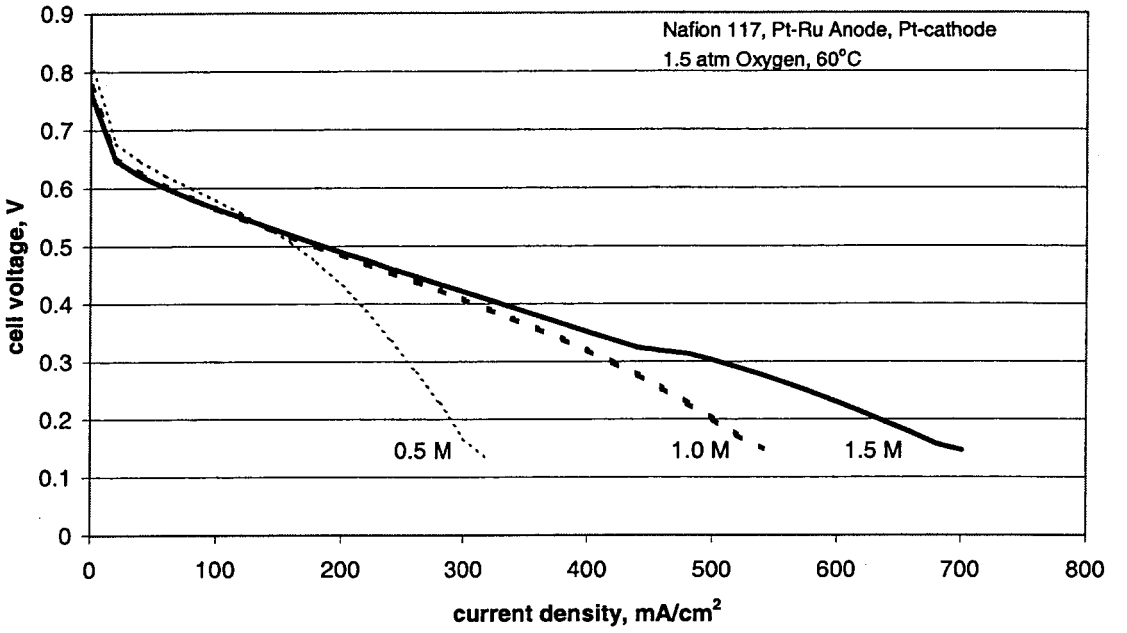

Figure 6. Effect of methanol concentration on DMFC that is not cathode limited.

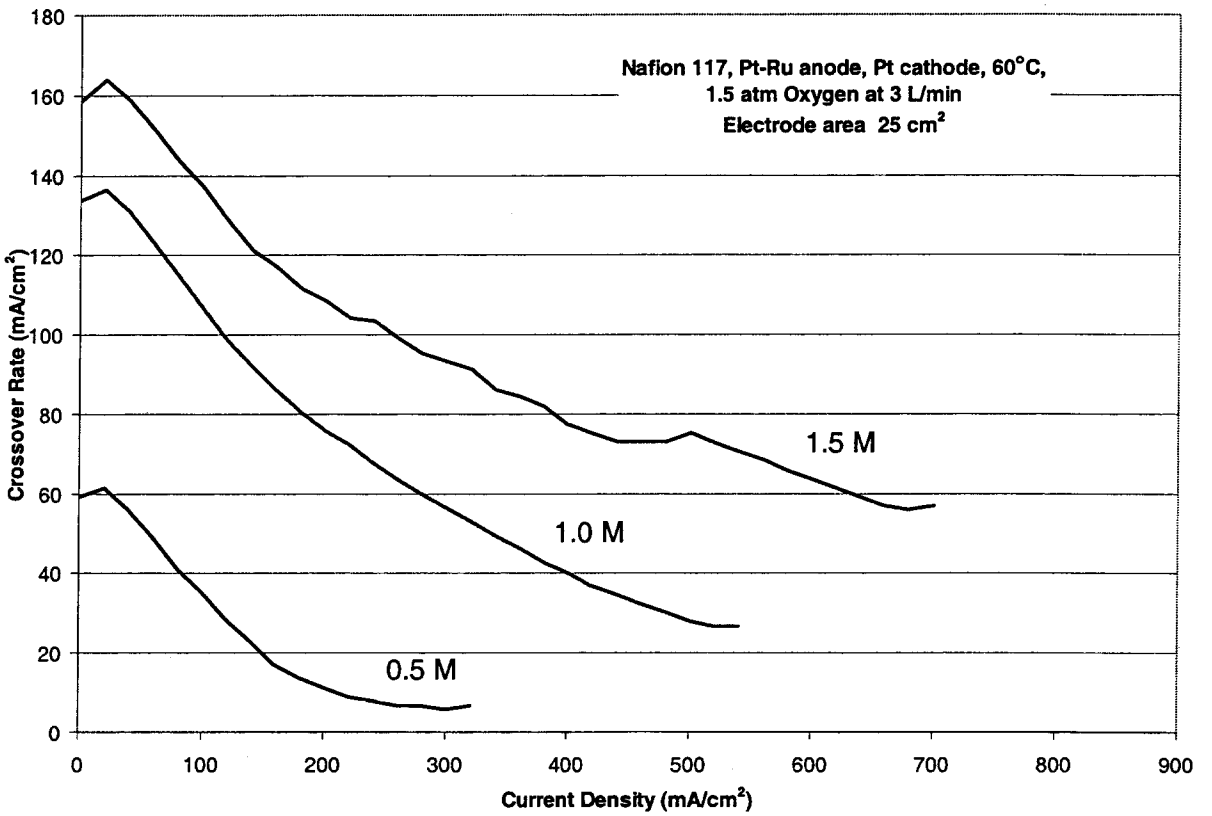

Figure 7. Dependence of methanol crossover rate on current density for a Nafion 117 MEA.

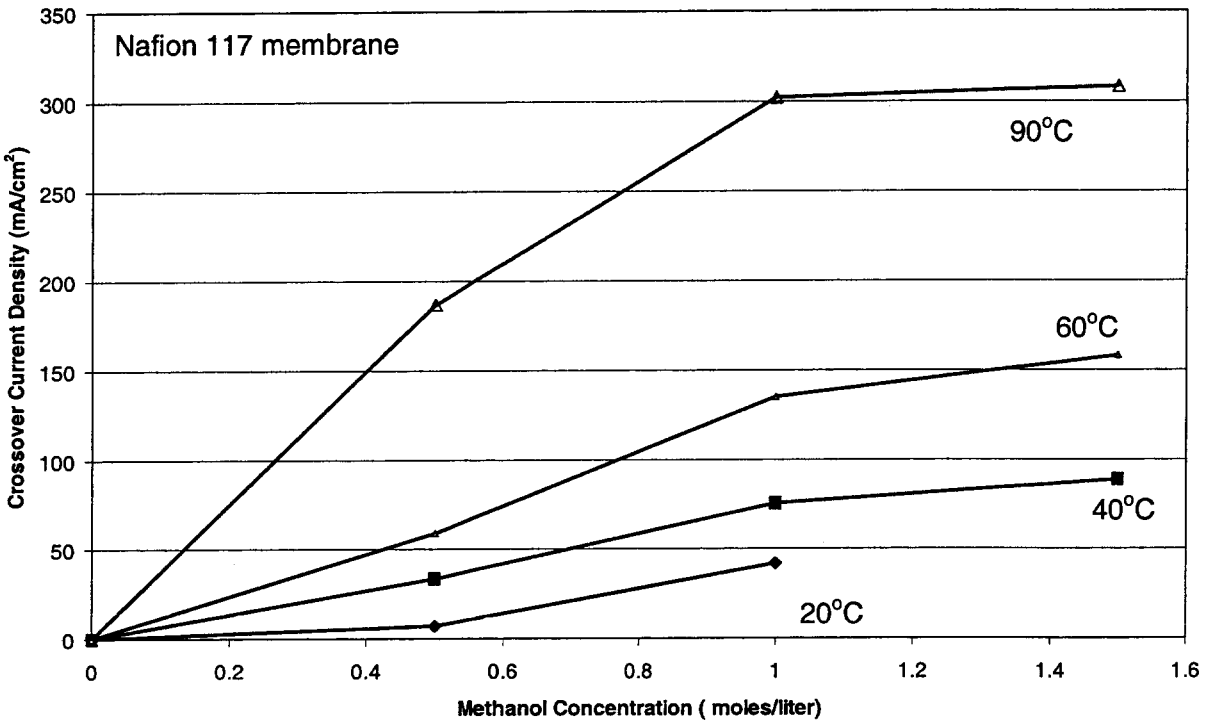

Figure 8. Dependence of crossover rate on concentration of methanol and cell temperature.

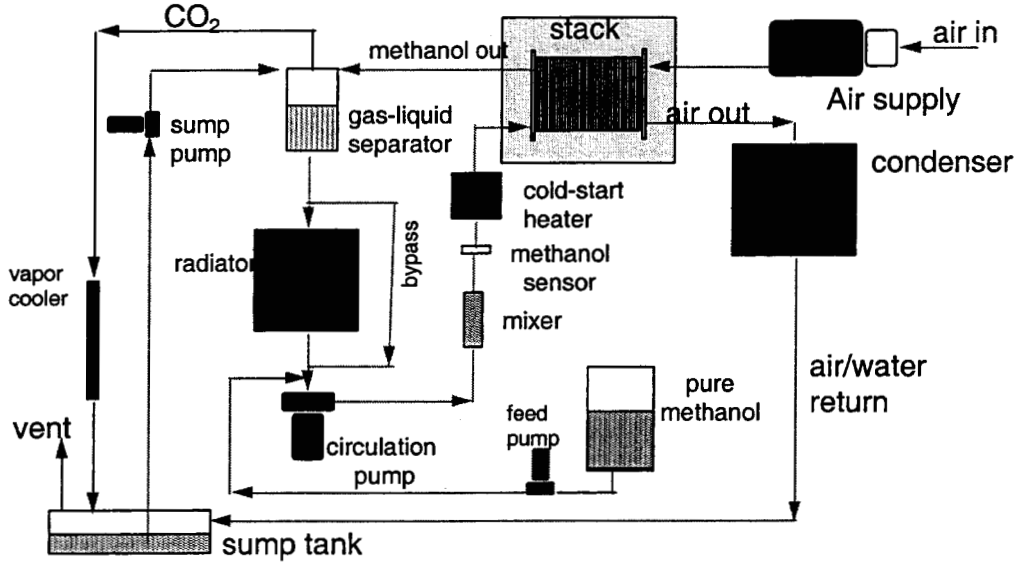

Figure 9. Schematic of a direct methanol fuel cell system for portable applications

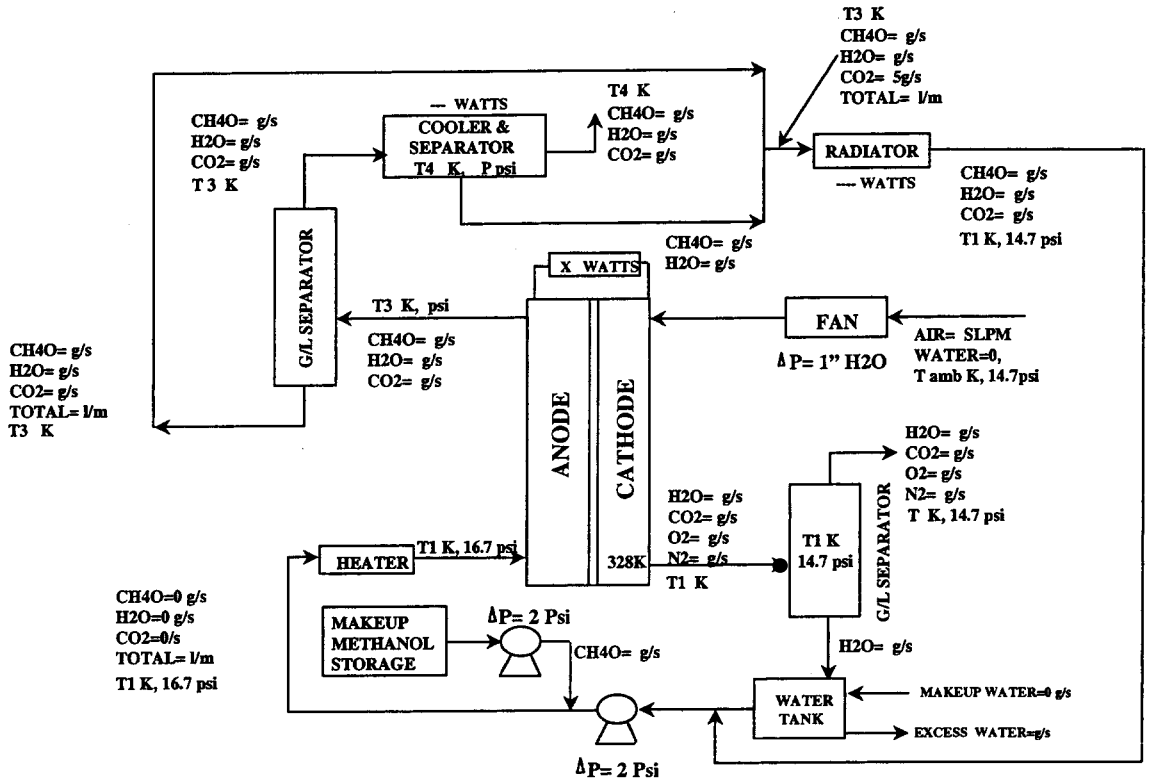

Figure 10. Thermal and Mass flow diagram that is obtained as a modeling exercise

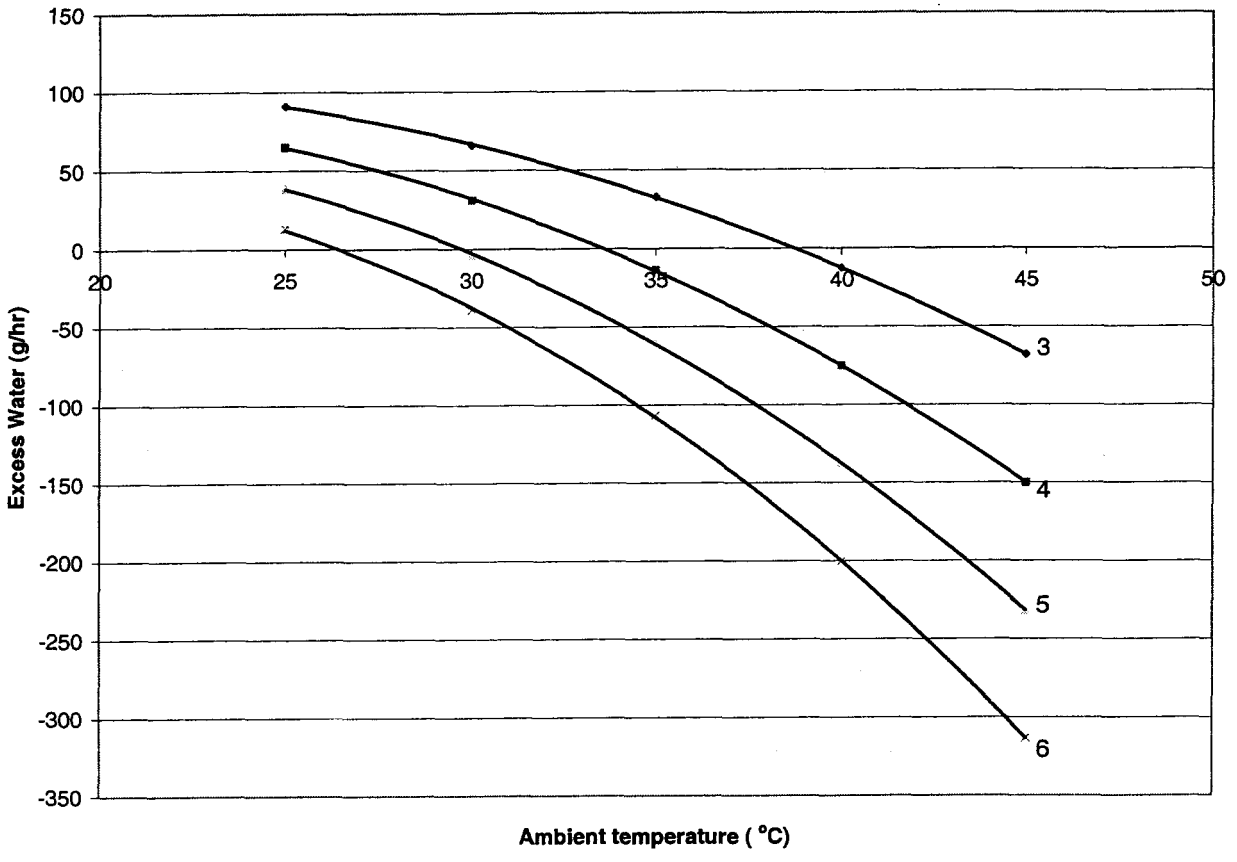

Figure 11. Water excess at various stoichiometric rates of airflow (indicated on the lines) at inlet (1 atm, RH=0%, Cathode exit = 60°C, 1M methanol, I = 100 mA/cm^2, power ~180 W, MeOH Flow rate 2L/min)

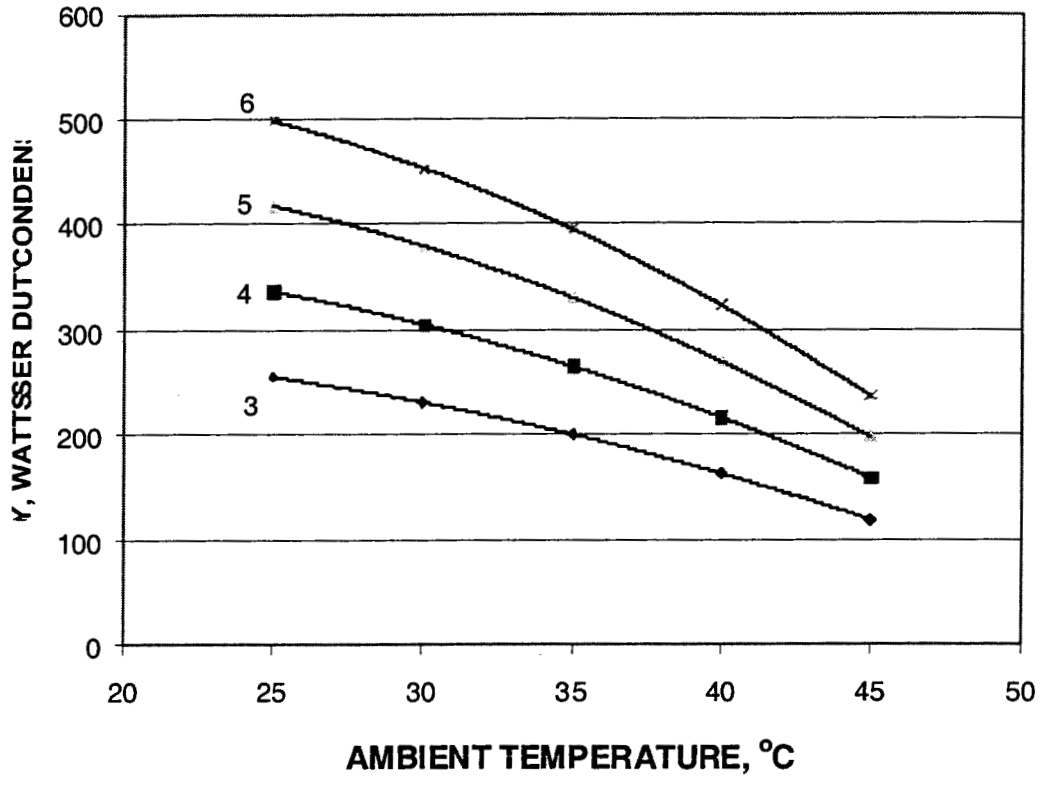

Figure 12. Condenser duty as a function of stoichiometric flow rate (RH=0%, Cathode exit = 60°C, 1M methanol, I = 100 mA/cm^2, power ~180 W, MeOH Flow rate = 2L/min)

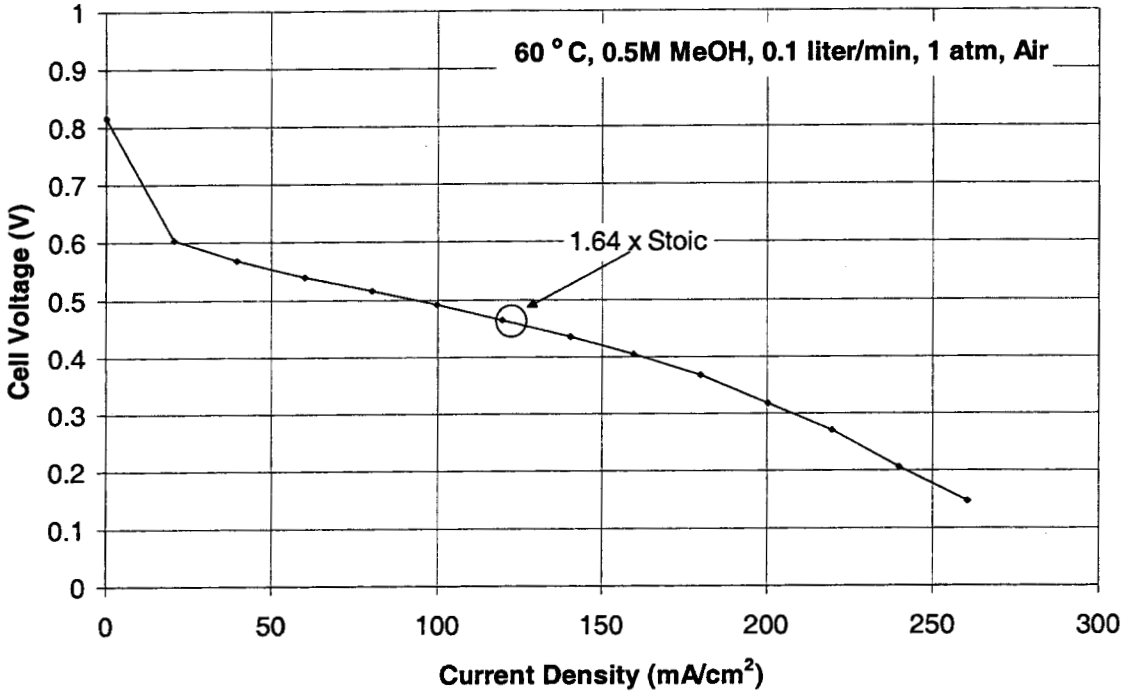

Figure 13. Performance of Nafion 117 MEA with improved cathode structure; active area, 25 cm^2.

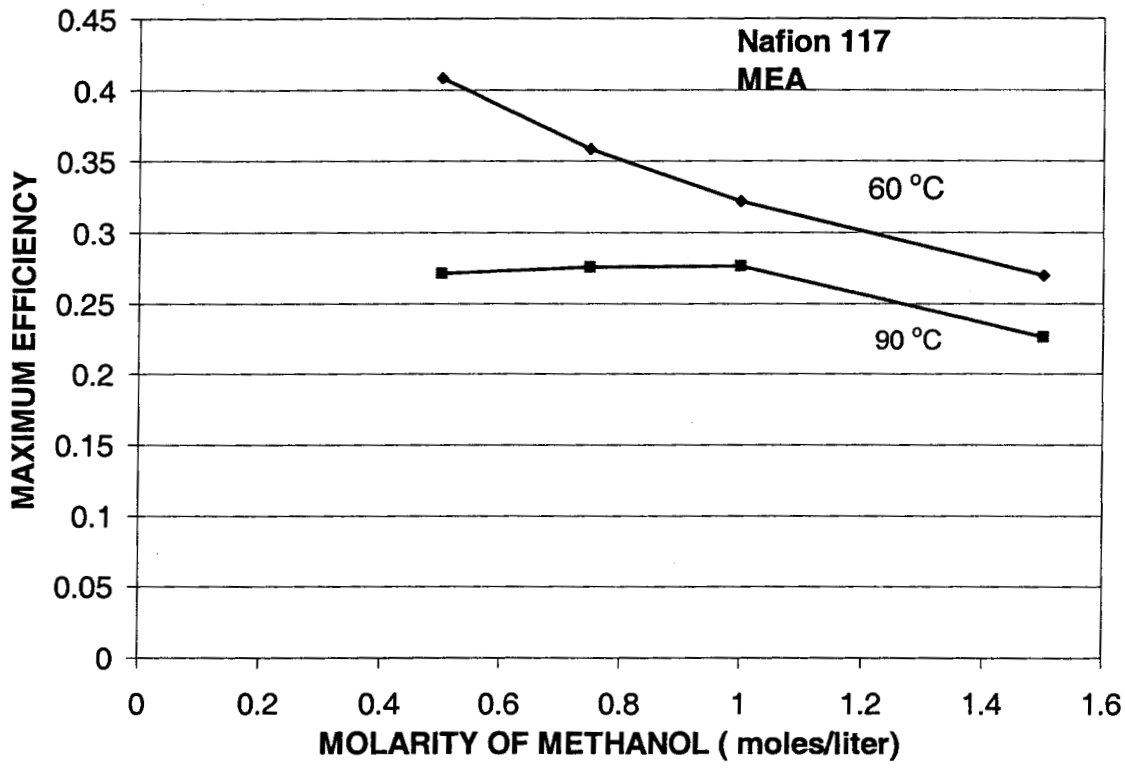

Figure 14. . Effect of methanol molarity on the current density attained at maximum efficiency

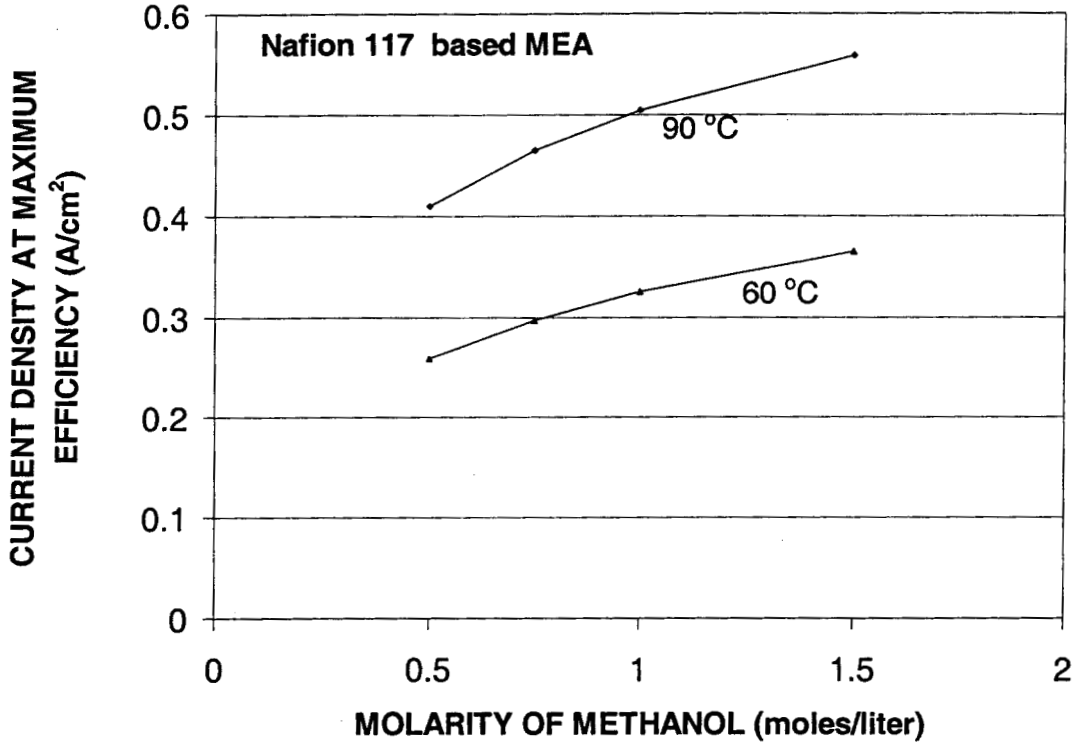

Figure 15. Dependence of maximum stack efficiency on molarity of methanol and temperature