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TITLE DIRECT METHANOL/AIR FUEL CELLS:  
SYSTEMS CONSIDERATIONS

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## Direct Methanol/Air Fuel Cells: Systems Considerations

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### ABSTRACT

Successful operation of a direct methanol/air fuel cell system depends upon appropriate integration of the fuel cell components and accommodation of the need for heat and mass transfer within the system. The features of the system that must be considered separately and in an interactive fashion are: (1) the physical state of the fuel feed stream, (2) electrode characteristics, (3) characteristics of the electrolyte, (4) product water removal, (5) heat transfer into or out of the stack, and (6) methanol loss modes. The operating temperature and pressure will be determined, to a large extent, by these features. An understanding of the component features and their interactions is necessary for initial system considerations for direct methanol/air fuel cells.

### INTRODUCTION

A direct methanol/air fuel cell would be an attractive device for providing power in a number of applications. It offers the direct use of a liquid fuel and thus alleviates the problems of carrying a gaseous fuel or of converting a liquid fuel to a gaseous fuel for use in the fuel cell. Therefore, the system would be simpler and more reliable. It could also offer decreases in weight and volume over systems that require the conversion of liquid fuels into gaseous fuel feed streams. In addition, methanol is easy to transport and present fuel distribution systems could readily be adapted to handle methanol.

As noted in recent reviews on direct methanol fuel cells (1,2), the main obstacle to achieving successful operation of such a fuel cell has been the inability to develop a suitable catalyst for the direct electrochemical oxidation of methanol. However, were the necessary catalyst developed, efforts could proceed to develop an operating fuel cell system. The following discussion covers some of the points which should be considered in the development of a direct methanol/air fuel cell system.

### SYSTEM CONSIDERATIONS

Successful operation of a direct methanol/air fuel cell system depends upon appropriate integration of the fuel cell components and accommodation of the need for heat and mass transfer within the system. Component requirements can

be dealt with separately; however, their interactions and other operational requirements must also be considered. A number of features of the system that can be considered separately and as they interact are: (1) the physical state of the methanol feed stream, (2) electrode characteristics, (3) characteristics of the electrolyte, (4) product water removal, (5) heat transfer out of or in to the stack, and (6) methanol loss modes. These features, taken as an integrated whole, will serve to define the operating temperature and pressure.

## 1. Methanol Supply to the Stack

The methanol fuel can be supplied to the fuel cell stack as either a liquid or a gas. Delivering the fuel as a liquid is the simplest mode. If the electrolyte is immobilized (contained in a matrix), the liquid methanol would be pumped into a plenum chamber behind the anode. If the system utilizes a recirculating electrolyte, the liquid methanol would be added to the electrolyte at some convenient point in the recirculation system. This assumes sufficient solubility of the methanol in the electrolyte to maintain the required supply of methanol at the anode face for any given reaction rate. The same assumption holds true for the immobilized electrolyte case.

If, because of system design, it is desirable to deliver the methanol to the fuel cell stack in the vapor phase, a means of vaporizing the methanol is required. In this case, the electrolyte would probably be immobilized and the methanol vapor would be fed into a distribution chamber at the back of the anode.

## 2. Electrodes

A. Anode - The anode catalyst developed must, of course, support complete oxidation of methanol and not be poisoned by or react with intermediates in the oxidation process. The structure of the anode is the important feature for the system. In the case with recirculating electrolyte, the anode structure must be such that the methanol-catalyst-electrolyte relationship necessary to support reaction rate demand can be maintained. In addition, the structure must not "weep" liquid through to the back of the electrode.

If the electrolyte is immobilized, the anode structure must allow the establishment of the catalyst-electrolyte interface. The structure must also be designed to allow the delivery of liquid or vapor phase methanol to the catalyst-electrolyte interface at rates sufficient to support reasonable power levels.

In any case, the anode structure must provide for the rapid removal of product  $\text{CO}_2$ .

B. Cathode - The cathode should provide good low pressure air operation. It is reasonable to assume that methanol will be soluble in any electrolyte used, therefore the cathode catalyst should be inert to methanol.

There is also the possibility that intermediate methanol oxidation products might desorb from the anode and migrate to the cathode, thus the cathode catalyst should be inert to these species.

It is most probable that product water will be formed at the cathode, therefore, the cathode structure must allow for the removal of this water with minimal or no loss of electrolyte.

### 3. Electrolyte

The electrolyte should support the complete oxidation of methanol. It should be inert to or, indeed, reject the product  $\text{CO}_2$ . Methanol should be sufficiently soluble in the electrolyte to support required reaction rates; however, the electrolyte should be inert to chemical reaction with methanol and any intermediate oxidation products. The physical state of the electrolyte may be a free, recirculating liquid, a liquid immobilized in a matrix, or a solid (such as a proton exchange membrane). The recirculating electrolyte could serve as the vehicle for the removal of heat and reaction products. Other means would be needed to provide these functions when the other types of electrolyte are used. In all three cases, the system would have to be designed to maintain the required water balance in the electrolyte. Water balance means not only maintaining a constant water content in the electrolyte but also ensuring, in the immobilized and solid electrolytes, that necessary water distribution is maintained and no parts of the electrolyte entity dry out or flood.

### 4. Product Removal

A. Water - It is assumed that product water will be formed at the cathode. If a recirculating electrolyte system is used, then the water may be removed from the electrolyte with devices similar to those used in mobile electrolyte alkaline fuel cell systems. Obviously, the water must be removed at a rate that maintains constant electrolyte concentration. This does not present any significant problems if done in an application that requires steady-state power delivery; however, for applications with transient power demands, control of the rate of water removal from the electrolyte may be difficult and may result in fluctuations in the electrolyte concentration. This might be tolerated over a narrow range but, certainly, large changes in electrolyte concentration could lead to unsatisfactory device performance. This latter situation might occur because of a slow response of the water removal strategy to dramatic changes in water production.

If the electrolyte is immobilized, the normal method for water removal is in the process air exhaust stream. Because an increase in power demand would be accompanied by an increase in process air flow, the response to the need to remove more product water would be rapid. The operating temperature and pressure of the fuel cell stack will determine if the product water is delivered to the gas side of the cathode as a liquid or a vapor. The physical state of the water could also be affected by the structure of the air electrode.

B. Carbon dioxide - Complete electrooxidation of methanol will result in carbon dioxide ( $\text{CO}_2$ ) formation at the anode. If the anode electrode in the recirculating electrolyte system is not porous, the  $\text{CO}_2$  will most likely be removed in the electrolyte stream. This means that both water and  $\text{CO}_2$  will have to be removed from the electrolyte after it exits the fuel cell stack. It is unlikely that both these products would be removed in the same device, thus, the system complexity would increase. Another possibility is that the  $\text{CO}_2$  could move through the electrolyte to the air electrode and exit through this porous structure into the process air stream. This could create difficulties either by further diluting the amount of oxygen available or by obstructing the access of the limited amount of oxygen to the catalyst.

It is anticipated that the anodes used with the immobilized or solid electrolytes will be porous. Therefore, the  $\text{CO}_2$  can pass through these electrodes and into the fuel stream. This stream can then be exhausted overboard or some means devised to remove the  $\text{CO}_2$  from the stream if recirculation of the stream is desirable. It is also possible that the anode exhaust stream may be used somewhere else in the system, for example, to provide heat to vaporize the methanol.

#### 5. Heat Transfer

Thermal regulation of the fuel cell stack at the selected operating temperature requires the incorporation of heat transfer schemes in the system. In most cases, more heat is generated within the stack by electrochemical inefficiencies than is required to maintain the stack temperature and, therefore, heat must be removed from the system. However, at power loads of half the stack rating or less, the heat generated is insufficient to maintain the stack temperature and heat must be added to the stack.

If the recirculating electrolyte mode of operation is used, heat may be removed or added by passing the electrolyte through suitable heat exchangers. With the immobilized or solid electrolytes, it may be necessary to have a thermal control loop passing through the stack with temperature control plates at appropriate positions within the stack. Some cooling may be accomplished with the process air or, if the product water appears as a liquid, by evaporation of the liquid into the cathode air exhaust. In any case, if heat must be supplied to the stack, this implies an external source of heat.

#### 6. Methanol Loss Modes

Loss of methanol means it cannot be used in the electrochemical reaction and thereby the system efficiency is lowered. Most of the common loss modes are the result of methanol entering one of the process streams and being removed from the fuel cell stack without reacting. In a recirculating electrolyte system, the methanol is dissolved in the electrolyte and is susceptible to being removed along with the product water or  $\text{CO}_2$ . It is also possible that the methanol could move through the air electrode and be carried

along in the cathode exhaust. Depending on the operating temperature, the methanol could distill out of the electrolyte and be lost in some part of the circulation loop.

In fuel cell stacks using immobilized or solid electrolytes, methanol could be carried out of the stack in either the anode or cathode exhaust streams. Neither of these streams is likely to be run as a closed loop; however, the methanol could be recovered in a condenser or some other device and returned to the fuel feed stream. Alternatively, if a source of heat is needed, these exhaust streams could be combined and used in a burner. If the stack is not carefully sealed, it is also possible that methanol could be lost from the edges of the electrolyte matrix or membrane.

#### 7. Temperature and Pressure

The operating temperature and pressure will be selected to optimize the performance of the system. This means that all of the features described above will have to be considered for each system design.

#### SUMMARY

In considering the design of a direct methanol/air fuel cell system, it is necessary to include not only the electrochemical subsystem (stack) but also the subsystems needed to achieve mass and thermal balances within the system. System operation depends upon the successful integration of all the components. To achieve this integration, the system design must identify and accommodate all interfaces, both in the fuel cell stack and external to it.