The Direct Methanol Liquid-Feed Fuel Cell

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BACKGROUND
Until the early 1990’s the idea of a practical direct methanol fuel cell for transportation and other applications was just that, an idea. Several types of fuel cells that operate under near ambient conditions were under development. The three types that operate at low temperature (<100°C) include: phosphoric acid type being implemented in transportation applications, e.g., in buses, alkaline liquid-electrolyte types presently in use in the shuttle and the PEM (Proton Exchange Membrane) type.

These low temperature fuel cells utilized gaseous hydrogen (H₂) directly or liquid fuel, e.g., methanol, reformed to hydrogen. Pure oxygen or oxygen in air served as the oxidant. The use of H₂ as a fuel presents some practical problems, such as storage system weight and volume as well as handling and safety issues especially for consumer and transportation applications. Indirect methanol fuel cells using reformers to convert methanol to H₂ add complexity as well as having potential for undesirable pollutants such as CO and some delay in load-following. The developments with direct and indirect fuel cells have been repotted by many and improvements continue to be made.

Methanol is an attractive alternative in view of its higher energy density (~5kWh/l compared with 2.6kWh/l for H₂, liq.), low cost, ease of handling and storage, and capability for distribution. Because recharging can be accomplished simply by adding liquid methanol to extend range with a minimum of delay.

Under a DARPA-sponsored program the fuel cell team at the Jet Propulsion Laboratory and the University of Southern California, Loker Hydrocarbon Institute, have patented a new non-polluting fuel cell technology that operates directly on a aqueous liquid methanol solution (Patent No. 5,599,638, Surampudi et al.). Since that time Giner Inc. has become a partner in the technology development for DARPA and other sponsors.

THE BASIC CELL CONCEPT
Since 1991, the team at the JPL, University of Southern California (USC) and Giner Inc. has been developing new materials and processes associated with the direct methanol fuel cell, its stack and system design [1-1 O].

The DMLFFC/PEM allows the direct use of a aqueous, low concentration (3%), liquid methanol solution as the fuel. Air (O₂) is the oxidant. The methanol and water react
directly in the anode chamber of the fuel cell to produce \( \text{CO}_2 \) and protons (H\(^+\)) that permeate the PEM and react with the oxygen at the cathode as shown in Figure 1.

The reactions are as follows:

**Anode:**

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 \uparrow + 6\text{H}^+ + 6e^- \quad (1)
\]

**Cathode:**

\[
6\text{H}^+ + 6e^- + \frac{3}{2}\text{O}_2 \rightarrow 3\text{H}_2\text{O} \quad (2)
\]

**Net Reaction**

\[
\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 \uparrow + 2\text{H}_2\text{O} \quad (3)
\]

The DMLFFC/PEM concept is shown in Figure 1. The heart of the technology is the central section that comprises the 0.020" thick Membrane Electrode Assembly (MEA). The MEA consists of the proton exchange membrane sealed between two carbon electrodes containing the 2-4mg/cm\(^2\) 50/50 Pt/Ru catalyst. 3\% aqueous methanol enters the anode chamber and is converted at the electrode interface to protons (H\(^+\)), electrons (e\(^-\)) and carbon dioxide (CO\(_2\)). The protons diffuse through the membrane and react at the cathode interface with air and the returning electrons to produce water. The catalyst at the cathode is Pt at 2-4 mg/cm\(^2\). The theoretical energy density of methanol is 5 kWh/liter compared with cryogenic hydrogen of 2.7 kWh/liter. 34\% or 1.7kWh/liter has been achieved in a 5 cell stack.

**SYSTEM CONCEPT**

Figure 2 is a closed system conceptual design. Its simplicity, compared with hydrogen or methanol-reformed systems, is due to liquid aqueous fuel circulation thus avoiding the mass and volume of existing humidifiers and thermal fins (estimated at every 5\(^{th}\) biplate) used to remove heat in the stack. The key advantage is that methanol is stored as a liquid in a manner similar to the liquid fuels presently in use, e.g., gasoline, diesel rather than hydrogen in high pressure cylinders.

Methanol from the fuel tank is mixed with recirculating water from the stack output to produce the desired concentration. The aqueous fuel is fed into a manifold that allows the fluid to flow past the anode in each cell. The aqueous fluid less the reacted methanol returns to the mixing tank for methanol addition. The carbon dioxide is released as a gas. Likewise, pressurized or unpressurized air flows past the cathode of each cell. The water produced is picked up in the air stream and returned to the mixing tank. Depending on temperature and application the water can be released as a vapor or liquid.

The fuel cell stack in this figure consists of any number of series connected cells. The electrochemical efficiency of the laboratory cells has improved to about 34\% when air is
used as the oxidant and operation is at 90°C. The efficiency is projected to exceed 45% with the use of advanced membranes and cell materials and designs. Cells have operated in the laboratory in excess of 3400 hours intermittently (equivalent to 170,000 miles at 50 mph) and 200 hours continuously without loss in performance.

ADVANTAGES OF A DMLFFC/PEM SYSTEM
In addition to the advantage of using a liquid fuel, the DMLFFC system has numerous advantages over the conventional fuel cell systems. The advantages include: a) no harmful emissions, b) elimination of fuel vaporizer, c) elimination of complex and voluminous humidification systems, d) more efficient thermal management systems, and e) significantly lower system complexity, size and weight. JPL and Giner have cooperated in designing complete DMLFFC systems for 10W, 40W, 150W and 5kW including all ancillary components for fuel, water, air and temperature balance. This work has resulted in eight new technology reports and two major patent applications.

PROGRESS
Aqueous methanol solution serves as the fuel for Direct Methanol, Liquid-Feed, Fuel Cell with Proton Exchange Membrane (( DMLFFC/ PEM) as the electrolyte. The oxidant can be compressed air or oxygen. The only products of reaction are water and carbon dioxide. Laboratory versions of the fuel cell operating directly on a 3% methanol/water solution at a temperature of 90°C have delivered a continuous output of 300 mA/cm² (50 A on a 4" x 6" electrode) at 0.5 V using air at 20 psig (0.55 V with oxygen). The peak power of 230 mW/cm² occurs at 600 mA/cm² (100 A on a 4" x 6" electrode). Using oxygen, the peak power was in excess of 320 mW/cm². The fuel cell also starts up at ambient temperature and has the same output at 60°C at 150 mA/cm² with unpressurized air.

JPL has recently completed assembly and test of three demonstration units for our sponsors. Unit 1 developed under the DARPA program is a 50 W fuel cell system that was operated continuously over a period of 2 hours to demonstrate its capability. Giner Inc. provided the stack and JPL assembled and tested the system. In this system pressurized air or oxygen was used as the oxidant. The 3% fuel composition is controlled by a methanol sensor which controls the flow of methanol to the mixing tank. Unit 2 was developed as a battery charger for the Army. It is a 4-10 W forced ambient pressure air stack that uses aqueous 3% methanol as the fuel. Ambient air flows through the stack and liquid water collects at its base to either be discarded or used to make up a fresh methanol solution. Unit 3 is a self-sustained hybrid enhanced DMLFFC battery charger system containing a second generation fuel cell, lithium-ion cells and an electronic control system. The fuel cell is activated when the voltage of battery drops below a preset level. It stops when the battery voltage rises to a preset level.

DTI Energy Inc., a California Company, has obtained a license from Caltech/JPL for commercialization of this technology. It has funded JPL through JPL’s Technology Affiliates Office to improve performance, develop a replacement MEA, and reduce cost. Support for the technology effort also includes the Army Research Office through the University of Minnesota to enhance the understanding and develop new materials to
improve performance. JPL has worked closely with its partners under the DARPA-funded programs to develop a compact high performance fuel cell system. The effort involved integration of off the shelf or fabricated pumps, controls, methanol sensor, mixing tank, and heat exchangers, and demonstration of performance in a benchtop configuration. USC, our second partner, is developing improved membranes with low methanol crossover and potentially lower cost than Dupont Nafion type membranes. For obvious reasons, this new technology is also being considered for a number of commercial applications including electric vehicles, marine and RV use, electronic and consumer devices, and remote and emergency power.

ACKNOWLEDGMENT
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REFERENCES: