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*Development and Demonstration of Advanced Technologies
for Direct Electrochemical Oxidation of Hydrocarbons
(Methanol, Methane, Propane)*

Final Report

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13. ABSTRACT (Maximum 200 words) Direct methanol fuel cells use methanol directly as a fuel, rather than the reformat typically required by fuel cells, thus eliminating the reformer and fuel processing train. In this program, Giner, Inc. advanced development of two types of direct methanol fuel cells for military applications. Advancements in direct methanol proton-exchange membrane fuel cell (DMPEMFC) technology included development of a Pt-Ru anode catalyst and an associated electrode structure which provided some of the highest DMPEMFC performance reported to date. Scale-up from a laboratory-scale single cell to a 5-cell stack of practical area, providing over 100 W of power, was also demonstrated. Stable stack performance was achieved in over 300 hours of daily on/off cycling. Direct methanol aqueous carbonate fuel cells were also advanced with development of an anode catalyst and successful operation at decreased pressure. Improved materials for the cell separator/matrix and the hardware were also identified.				
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1.0 INTRODUCTION

Giner, Inc. conducted a program to advance the development of direct methanol oxidation fuel cells for various military applications, including unmanned undersea vehicles, soldier integrated protective ensembles and armored vehicles. Direct methanol fuel cells electrochemically oxidize methanol, using it directly as a fuel, rather than the reformat typically used in fuel cells, thus eliminating the weight, volume, cost and complexity of a reformer and the associated fuel-processing train from the fuel cell system. This program focused on development of two types of fuel cells for use with direct methanol: the proton-exchange membrane fuel cell (PEMFC) and the aqueous carbonate fuel cell (ACFC).

Development of the direct methanol PEMFC was conducted in conjunction with the Jet Propulsion Laboratory (JPL) and with several universities involved in basic research. The aims of this program were to provide assistance to JPL and the Universities by: (a) developing methodology to fabricate electrode structures for University-developed catalysts; (b) evaluate advanced catalysts and electrolytes in complete fuel cells; and (c) developing scale-up technology to fabricate and demonstrate operation of a multi-cell stack of practical area.

Development of the direct methanol ACFC was conducted by Giner, Inc. The ACFC uses an alkaline, CO₂-rejecting electrolyte, and when operated in the Giner, Inc. mode with CO₂ recycled to the cathode, has shown considerable promise for direct methanol oxidation. Prior development focused on operation at ~160°C and 120 psig, which may not be desirable for military applications; however, previous studies had shown that efficient cell operation at lower temperature and near atmospheric pressure may be possible with further development. Thus this program focused on development of advanced methanol oxidation catalysts and electrode structures and an improved matrix, to provide enhanced performance at lower temperature and pressure.

2.0 SUMMARY OF RESULTS

2.1 Direct Methanol PEMFC

A major focus of the direct methanol PEMFC development was preparation and evaluation of advanced catalysts, including catalysts developed by Giner, Inc., JPL and the Universities, and development of efficient anode structures for use with these catalysts. Catalysts evaluated included compositions of Pt, Pt-Ru, Pt-Ru-Sn, and Pt-Sn of various ratios, both supported on carbon blacks and unsupported.

During this program, Giner, Inc. developed a Pt-Ru anode catalyst and an electrode structure for use with this catalyst that provided some of the highest direct methanol PEMFC performance reported to date. This was confirmed in testing by JPL and International Fuel Cells Corp. of Giner, Inc. membrane-electrode assemblies (MEAs). As shown in Figure 1, a direct liquid methanol-O₂ fuel cell achieved performance of 636 mV and 567 mV (terminal) at 100 and 200 mA/cm², respectively, at 80°C in testing at Giner, Inc. The fuel to this cell was 1.0M methanol in water; addition of acid to the fuel stream, as required by previous direct liquid methanol fuel cells, is not required by the Giner, Inc. cell due to the unique anode structure. This performance was obtained in a laboratory fuel cell with an active area of 40 cm².

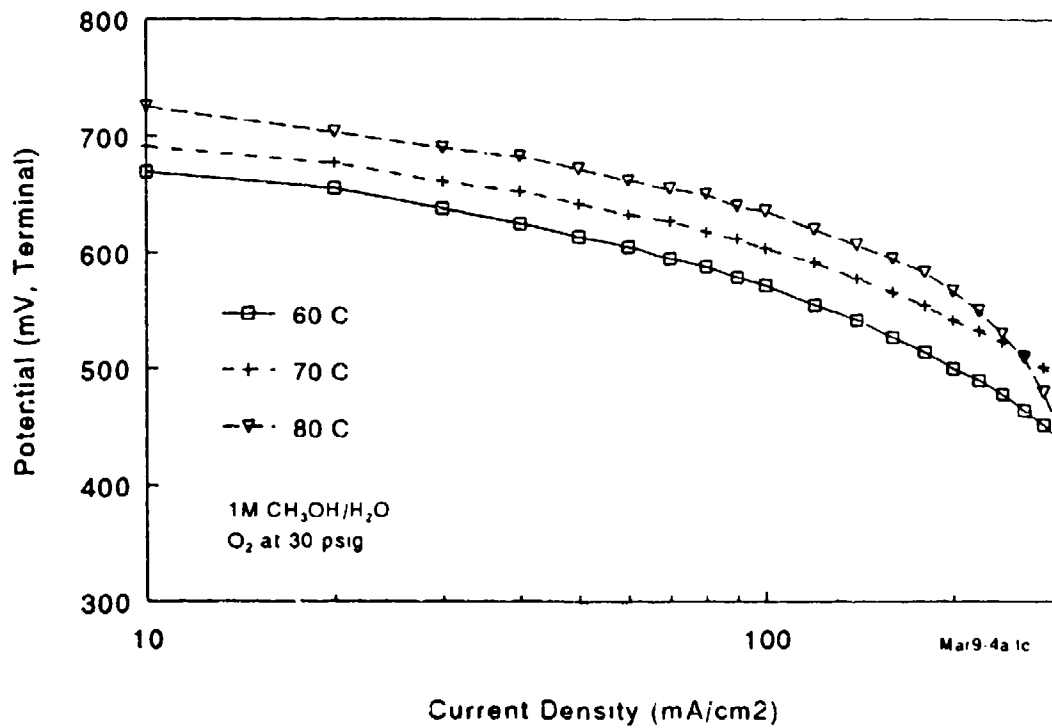
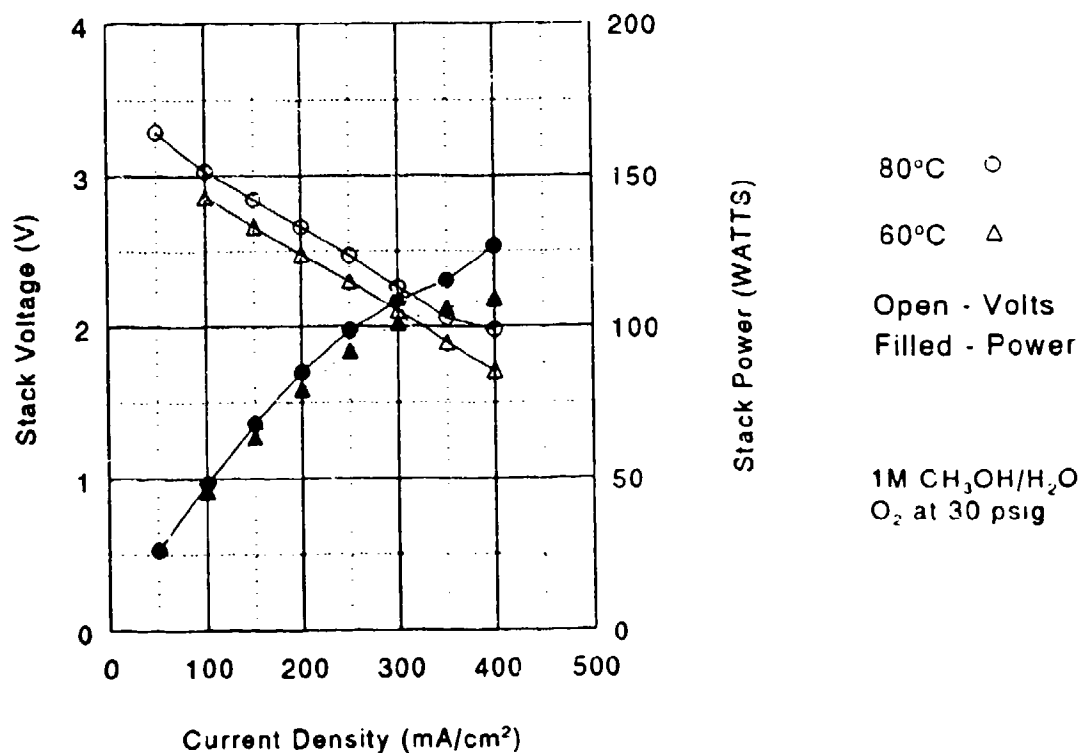


Figure 1. Performance of a Direct Methanol PEMFC (40 cm² active area)

A second major focus of this program was to demonstrate the ability to scale up the direct methanol PEMFC technology by increasing the active area of individual cells and by developing a multi-cell stack. Initially, scale-up of a single cell by a factor of four, from 40 cm² to 160 cm² active area, without loss of fuel cell performance was demonstrated. We also fabricated MEAs with an active area of 258 cm². The scale up effort culminated in successful operation of a 5-cell stack, with each cell having an active area of 160 cm². As shown in Figure 2, this direct methanol PEMFC stack produces greater than 100 Watts of power at both 60 and 80°C. This stack has also demonstrated substantial life and the ability to withstand on/off cycling with stable performance. During the course of the program, the stack was run primarily at 100 mA/cm² and 60°C for approximately 200 hours, with 7-10 hours of operation/day; life testing is continuing under Giner, Inc. funding. Figure 3 shows stack performance to date; after approximately 300 hours of cumulative running time, the stack voltage at 100 mA/cm² is slightly higher than the initial voltage and performance is quite stable. This life performance of a stack of practical size demonstrates that the direct methanol PEMFC with further development is a feasible power source for various military applications.



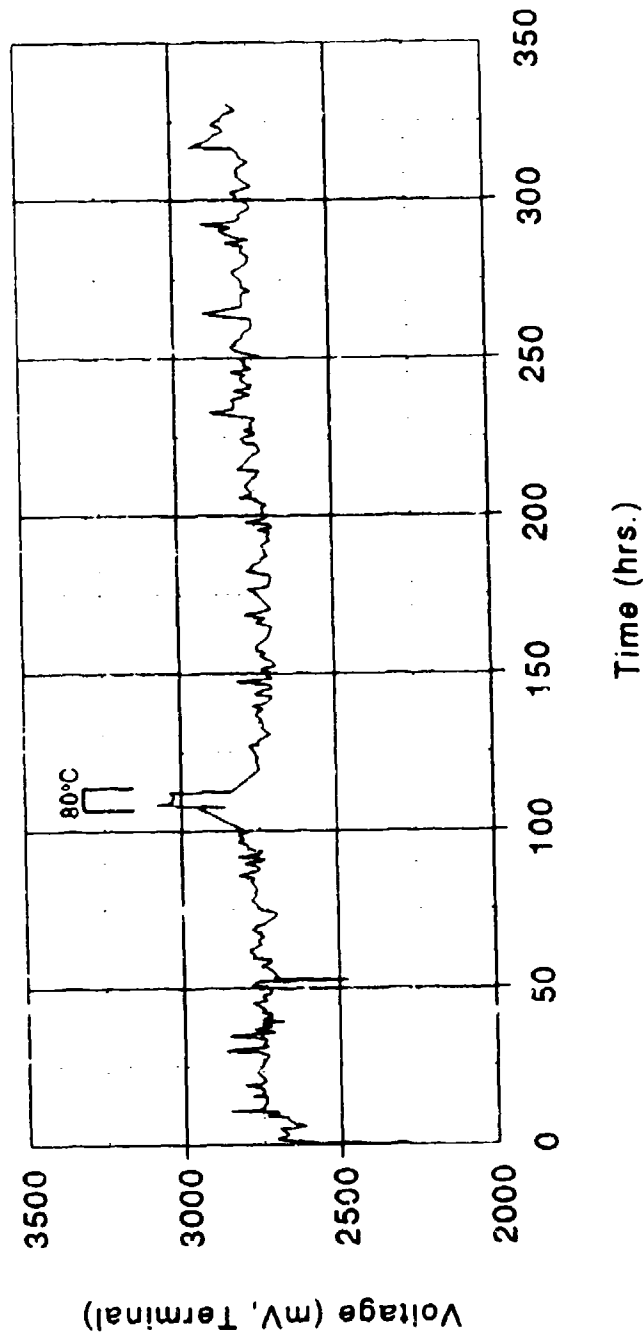
PEMFC-HD121

Figure 2. Power and Voltage of the Giner, Inc. Direct Methanol PEMFC 5-Cell Stack

Additional efforts during the course of the program were aimed at a) identification of cathode structures compatible with anode liquid feed operation and b) evaluation of alternative fuel cell electrolyte membranes. A large quantity of water is present at the cathode of a DMPEMFC as a result of protonic pumping, oxygen reduction, and methanol crossover with resulting chemical oxidation. Brief studies identified a cathode structure which could function effectively in the presence of this water and methanol.

The bulk of the testing in this program, including that shown in Figures 1, 2 and 3, was obtained using Nafion 117 as an electrolyte. Due to the high rate of methanol crossover from anode to cathode with this membrane, alternative membranes such as Nafion 324, Nafion 350 and Nafion 120 were evaluated. Use of these membranes slightly decreased methanol crossover, but also caused a 30- to 60-mV drop (at 100 mA/cm²) in DMPEMFC performance, relative to that of Nafion 117.

The major conclusion drawn from our DMPEMFC testing is that this is a very promising fuel cell technology and is a feasible power source with further development for various military applications. Additional efforts are required to further develop efficient cathode structures and alternative membranes which limit the quantity of methanol permeating from anode to cathode.



1M CH₃OH
 30 psig O₂
 60°C
 100 mA/cm²
 160 cm²/Cell

PEM5C1-2.1c, HD121

Figure 3. Life Plot of the Direct Methanol PEMFC 5-Cell Stack

2.2 Direct Methanol ACFC

Anode catalyst development was also a major focus of the direct methanol ACFC studies. A number of binary and ternary Pt-based catalysts, supported on carbon black, were evaluated as replacements for the standard Pt/Vulcan XC-72 anode catalyst using an ACFC half-cell technique in addition to fuel cell testing. In contrast to the PEMFC, the direct methanol ACFC uses vaporized methanol rather than liquid methanol as the fuel. Superior performance was achieved by catalysts with various ratios of Pt:Ru, supported on Vulcan XC-72. At the standard ACFC operating conditions of 165°C, 120 psig with an anode feed of 25% methanol/29% H₂O/46% N₂ and a cathode feed of 50% O₂/50% CO₂, a cell with a supported Pt-Ru catalyst achieved a terminal voltage of 667 mV at 100 mA/cm², compared to typical performance with a Pt/Vulcan catalyst of 600 mV. The ACFC performance with the Pt-Ru/Vulcan catalyst is the highest direct methanol fuel cell performance reported to date.

This program was successful in decreasing the operating pressure of the direct methanol ACFC without a significant decrease in performance. Reducing cell operating pressure from 120 psig to 80 psig did not change cell voltage, and a further reduction to 40 psig resulted in a loss of ~60 mV at 100 mA/cm², yielding a voltage of 650 mV.

Other aspects of direct methanol ACFC development addressed in this program were: a) identification of a separator/matrix material which provides performance similar to that obtained with the standard asbestos matrix, while providing increased cell life; and b) identification of a corrosion-resistant material to replace the Ni cell hardware. Preliminary investigations indicate that SiC with a suitable binder provides promising direct methanol ACFC performance. Further testing is required to optimize the composition of this matrix and to evaluate its performance and life. Further testing is also required to determine long-term corrosion resistance of promising cell hardware materials.

The direct methanol ACFC is a very promising fuel cell technology, with the best fuel cell performance on direct methanol reported to date and the potential to be relatively low cost. However, this technology is less advanced than that of the direct methanol PEMFC and further development is required to determine its feasibility for military applications.

3.0 PUBLICATIONS AND TECHNICAL PRESENTATIONS

J.A. Kosek, C.C. Cropley, G. Wilson, A.B. LaConti, S. Narayanan, E. Vamos, S. Surampudi and H. Frank, "A Direct Methanol Fuel Cell," Presented at the 28th Intersociety Energy Conversion Engineering Conference, Aug. 8-13, 1993, Atlanta, GA, and published in the conference proceedings.

J.A. Kosek and A.B. LaConti, "Methanol Oxidation Fuel Cells," Presented at the NSF/DOE Fuel Cell/Electric Automobile Workshop, Dec. 14, 1993, Washington, DC, and published in the conference proceedings.

J.A. Kosek, "A Direct Methanol Oxidation PEM Fuel Cell," Presented at DOE Fuel Cells for Direct Methanol Oxidation Review Meeting, April 26, 1994, Baltimore, MD.

S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakesh and G.A. Olah, "Advances in Direct Oxidation Methanol Fuel Cells," *Journal of Power Sources*, **47**, 377-385 (1994).

Quarterly progress reports were submitted to the Jet Propulsion Laboratory (JPL) for inclusion in the consolidated Quarterly Report issued by JPL to ARPA.

4.0 PARTICIPATING SCIENTIFIC PERSONNEL

A.B. LaConti and J.A. Kosek - Principal Investigators; C.C. Cropley, G. Wilson, J. Unger, S. McCatty, A. Griffith, and M. Hamdan.

5.0 REPORT OF INVENTIONS

- (1) "Membrane and Electrode Assembly for a Direct Methanol Fuel Cell" (Patent Application Prepared for Filing)
- (2) "Proton-Exchange Membrane Fuel Cell Using Composite Membranes" (Patent Disclosure on File at Giner, Inc.)