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"DIRECT METHANOL FUEL CELLS FOR TRANSPORTATION APPLICATIONS"

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Contract DE-AC08-96NV11984

Quarterly Technical Report

FCR-14719

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Prepared for

U. S. Department of Energy
Nevada Operations Office
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Section I. Introduction

The purpose of this research and development effort is to advance the performance and viability of direct methanol fuel cell technology for light-duty transportation applications. For fuel cells to be an attractive alternative to conventional automotive power plants, the fuel cell stack combined with the fuel processor and ancillary systems must be competitive in terms of both performance and costs. A major advantage for the direct methanol fuel cell is that a fuel processor is not required. A direct methanol fuel cell has the potential of satisfying the demanding requirements for transportation applications, such as rapid start-up and rapid refueling. The preliminary goals of this effort are: (1) 310 W/l, (2) 445 W/kg, and (3) potential manufacturing costs of $48/kW.

In the twelve month period for phase I, the following critical areas will be investigated: (1) an improved proton-exchange membrane that is more impermeable to methanol, (2) improved cathode catalysts, and (3) advanced anode catalysts. In addition, these components will be combined to form membrane-electrode assemblies (MEA's) and evaluated in subscale tests. Finally a conceptual design and program plan will be developed for the construction of a 5 kW direct methanol stack in Phase II of the program.

There are three principal participants in this program: (1) International Fuel Cells, (2) the University of Connecticut, and (3) the University of Southern Mississippi. The University of Southern Mississippi will develop methanol impermeable membranes, the University of Connecticut will develop methanol impermeable membranes and a redox couple. International Fuel cells will develop advanced catalysts for direct methanol fuel cells, conduct subscale testing of all membranes and catalysts, develop a conceptual design for a 5 kW stack, and manage the overall program. The program is broken into six tasks. Each is discussed in more detail below.

Task 1. Development of Methanol Impermeable Membranes – The objective is to develop a proton exchange membrane with reduced methanol crossover and adequate electrical conductivity. Three approaches are planned, the first is the synthesis of composite membrane. Matrix-Nafion composite structures will be investigated and the characteristics of the interaction between Nafion and the composites will be determined. Porous materials, such as Teflon, polyvinylidene fluoride, polycarbonate, and alumina, that retain Nafion in a small pore matrix with pore sizes ranging from 0.03-0.6 µm. will be considered. The resulting membranes shall be evaluated for methanol permeability and proton conductivity.

The second approach is synthesis of crosslinked membranes. Means to reduce the solvent (water/methanol) content of the membrane by crosslinking sulfonic acid polymers with polyamines to compress the structure of the membrane will be investigated. Amine crosslinked structures will be synthesized and evaluated for methanol permeability and proton conductivity.

The final approach is synthesis of dendrimer-modified membranes. Means to insert dendrimers into perfluorosulfonate ionomers to prevent methanol transport through the resulting membrane will be investigated. Dendrimers up to the fifth generation covering a range of sizes and functionality shall be synthesized. Solution phase processes and melt processing technology shall be employed to insert the dendrimers into the ionomers. After the dendrimers have been synthesized and processed into an ionomer film, the mechanical properties, methanol permeability, and proton conductivity of the film shall be determined.

Task 2. Advanced Catalysts for Direct Methanol Fuel Cells – The objective is to develop anode catalysts with reduced polarization for the oxidation of methanol and cathode catalyst with improved

oxygen reduction activity and lower adsorption of methanol. Three activities are planned to develop advanced, higher performing anode catalysts and methanol tolerant cathode catalysts.

Advanced platinum-tantalum alloy catalysts for improved selectivity for methanol oxidation reaction rates and resistance to carbon monoxide poisoning will be investigated. The catalyst(s) will be evaluated in direct methanol fuel cells and their performance characterized as a function of the degree of alloying, stability of the alloy under fuel cell operating conditions, chemical composition, and methanol oxidation rate.

Redox couple catalysts for the oxidation of methanol or carbon monoxide will be identified. Methods of depositing and immobilizing the redox catalysts in polymer films shall be established. Electrode structures that incorporate a co-catalyst, such as gold or platinum, shall be investigated. These electrodes shall be characterized with regard to the efficiency of the redox and co-catalyst to oxidize methanol at fuel cell operating conditions.

Cathode catalysts with improved methanol tolerance will be identified. Catalysts such as alloys of platinum/cobalt/chromium and platinum/iridium supported on carbon will be investigated. The alloy catalyst with the greatest resistance to methanol adsorption shall be formed into membrane electrode assemblies and evaluated in a DMFC.

Task 3. Direct Methanol Fuel Cell Testing – The objectives of this task are to evaluate the catalyst and membranes developed in task 1 and 2 in subscale fuel cells. The results will be used in the conceptual design of the 5 kW stack. A standard direct methanol MEA shall be tested to establish a baseline performance. Membranes developed in Task 1 showing reduced methanol permeability in out-of-cell tests shall be fabricated into MEAs for testing in fuel cell(s). These tests shall quantify methanol crossover, resistance losses, and impact on electrode performance. The best available membrane and the best catalysts from Task 2 shall be fabricated into MEAs and demonstrated in fuel cell tests.

Task 4. Performance Analysis and Conceptual Design – The objective of this task is to establish design criteria for an advanced direct methanol fuel cell stack for automotive applications. A conceptual design of the fuel cell that meets the weight and volume goals established in the solicitation shall be prepared.

Task 5. Demonstration Plan – The objective of this task is to develop a detailed plan for the Phase II construction and demonstration of the advanced direct methanol fuel cell for DOE approval. The plan shall include a description of the required tasks with a schedule and an estimate of the effort required to complete the plan.

Task 6. Management and Reporting – This task provides for management and documentation of the program. The management function performs the necessary activities to ensure that contract and technology objectives are achieved on time and within budget.

Section II TECHNICAL PROGRESS SUMMARY

Task I. Development of Methanol Impermeable Membranes

Composite Membrane Synthesis – UCONN's objective is to develop composite membranes with Nafion electrolyte in order to reduce methanol transport and still maintain good ionic conductivity. Three approaches were active during this reporting period: (1) PVDF/Nafion blends, (2) composite membranes with alumina, and (3) incorporation of phosphotungstic acid in Nafion.

Initially, we attempted to impregnate porous polyvinylidene fluoride (PVDF) membranes with Nafion. Purchased PVDF membranes were found to be too thick to impregnate fully. Consequently, membranes were solution cast using mixtures of Nafion and PVDF dissolved in DMF. Membranes were prepared using 25, 37.5, 50, 62.5, and 75 vol% Nafion. X-ray analyses of these mixtures indicated that both the Nafion and PVDF retain crystallinity. In out of cell tests, large reductions in methanol flux were found with a two mil membrane thickness compared to the seven mil thick Nafion 117 prior to the hydrogen peroxide treatment to clean the membrane and sulfuric acid treatment to acidify the membrane, but the conductivity was very poor. After treating the membrane, the conductivity was greatly improved but the methanol flux reduction was not as large. We were concerned that the hydrogen peroxide treatment may be too severe and that an ionic contact resistance is present in these tests. Since the conductivity is measured at room temperature and a contact resistance has been found to be present, samples were sent to IFC to evaluate in full-cell at temperature.

Two membranes were fabricated and submitted to IFC for cell testing. These membranes were a 0.5 mil thick, 50 vol% Nafion/50 vol% polyvinylidene fluoride (PVDF) composite, and a 2 mil thick 75 vol% Nafion/25 vol% PVDF composite. The higher resistance mentioned above was the reason for the fabrication of thinner membranes using the PVDF. However, the 0.5 mil membrane was damaged during the lamination process and could not be tested. Cell testing of the second composite Nafion/polyvinylidene fluoride (PVDF) membrane at IFC resulted in a 301 mA/cm^2 (280 ASF) equivalent methanol flux for a membrane of this type of only 2 mils thickness compared to a methanol flux of 194 mA/cm^2 (180 ASF) for a Nafion 117 membrane of 7 mils thickness. The composite membrane also had a lower resistive loss than the Nafion 117. The PVDF composites showed a larger methanol flux reduction in out-of-cell laboratory tests but a higher ionic resistance. The pressing temperature of 330° F used for pressing the membrane-electrode assembly (MEA) may have been too high and may have melted the PVDF and significantly altered the membrane properties.

Three additional Nafion/polyvinylidene fluoride membranes were prepared and submitted to IFC for cell testing in order to provide guidance in optimizing the Nafion content, thickness, and MEA pressing temperature. The first was a 50% Nafion, 2 mil thick membrane with a suggested 166°C (330° F) pressing temperature for the MEA. The second was a 75% Nafion, 2 mil thick membrane with a 132°C (270°F) pressing temperature. The third was a 75% Nafion, 4 mil thick membrane with a 166°C (330° F) pressing temperature.

Cell testing of the composite 75 vol% Nafion/25 vol% polyvinylidene fluoride (PVDF) membrane resulted in a 258 mA/cm^2 (240 ASF) equivalent methanol flux for a membrane of this type of 4 mils (0.010 cm) thickness compared to a methanol flux of 194 ma/cm^2 (180 ASF) for a Nafion 117 membrane of 7 mils (0.018 cm) thickness. The composite membrane also had a 29 mV resistive loss at 108 ma/cm^2 (100 ASF) compared to 19 mV for Nafion 117. This membrane was pressed into the membrane-electrode assembly (MEA) at 270°F (132°C), below the melting point of the PVDF. Although the permeability of methanol was reduce by about 25%, the expected methanol flux reduction based on laboratory data was much larger than this. Several additional Nafion/polyvinylidene

fluoride membranes are being prepared and will submitted to IFC for cell testing in order to provide guidance in optimizing the Nafion content, thickness, and MEA pressing temperature.

A 7 mil thick 16 vol% alumina/84 vol% Nafion composite was prepared and sent to IFC for full-cell testing. The cell had very high iR and would not hold load. Since the performances the Nafion-alumina composite membrane was much below the anticipated levels when incorporated in fuel cells at IFC, one of these cell membrane-electrode assemblies (MEA's) was obtained from IFC for post-test analyses at UConn. Prior to delivery, a sample of this type membrane resulted in a resistance of 2.4 Ω-cm^2 after the peroxide and acid wash. This resistance translates into a 0.24 volt iR drop at 100 mA/cm^2. This high a loss was considered acceptable because the resistance was measured at room temperature and membrane-electrode contact losses were though to be present in the rig used to measure the resistance. The MEA as received from IFC had a resistance of 9.9 Ωcm^2, equivalent to an iR drop of 0.99 volts at the same current density. This larger iR could explain the poor cell performance. The membrane in this MEA was not washed in peroxide and acid, and no Nafion was present in the electrodes. To improve the membrane conductivity and reduce contact losses, Nafion was added to the electrodes and the package was washed in peroxide and acid. After this treatment, the resistance was reduced by more than a factor of 10 to 0.96 Ωcm^2, a value that would result in a cell iR of 0.096 volts at 100 ma/cm^2. The actual cell iR would be much less than this value because of the higher cell operating temperature. Because of these post-test results, a new membrane of this type will be prepared and submitted to IFC for another cell test with a suggested MEA fabrication procedure.

Nafion composite membranes were also prepared using zirconium phosphate and phosphotungstic acid as the filler material because of its proton conductivity. These acid are being evaluated because they may provide proton conductivity to the Nafion filler and allow higher temperatures of operation. One membrane containing zirconium phosphate was submitted to IFC for evaluation in a cell. A second membrane containing phosphotungstic acid was submitted to IFC for evaluation in a cell. In this case, the Nafion/phosphotunstic acid composite was supported in a Teflon structure. This type membrane must be tested using fuel in the vapor form to avoid washing the phosphotungstic acid from the membrane.

Chemically Modified Proton Exchange Membrane – Dr. Johna Leddy at the University of Iowa is evaluating polyamine crosslinked sulfonic acid polymers to reduced methanol transport while still retaining good ionic conductivity. Either a layer of polyallyl amine hydrochloride was cast onto the surface of a Nafion membrane or a film of Nafion and polyallylamine hydrochloride were cocast. The cocast films had no mechanical stability and did not form satisfactory membranes. The membranes formed by casting polyally amine onto a Nafion film sustained proton conduction, however, the polyallyl amine adlayer is water soluble and dissolved from the Nafion surface. Insoluable membranes that sustain ion conduction were formed by crosslinking the polyallyl amine adlayer. All membranes were 7 mils thick. Membranes were fabricated consisting of a thin layer of Nafion crosslinked polyallylamine applied to one surface of a Nafion 117 membrane. Four of these membranes were submitted to IFC for cell testing evaluation in a fuel cell (see Table 1) indicated that some of these membranes showed a large reduction in methanol crossover with only a small change in resistance.

Table 1. Cell Testing Evaluation		
Membrane	iR(mV) at 100 ASF	Crossover (% CO2 in Cathode Exhaust
Baseline Nafion 117	20	0.55
cold/cocast	55	0.25
cold/cocast	24	0.95
heat/cocast	23	0.30
heat/cocast	22	0.30

Dendrimer-Modified Membrane Synthesis – USM is developing membranes of Nafion/poly(propylene imine) dendrimers in order to maintain ionic conductivity while reducing methanol flux. In addition to these propylene imine dendrimers, sulfonated dendrimers and blends of polyvinylidene fluoride (PVDF) were used to prepare membranes. Alkanesulfonation of the second generation dendrimer was performed to decrease the resistivity of the Nafion/dendrimer blend while maintaining the low methanol crossover values. The second generation dendrimer was selected as it afforded the most promising results from fuel cell testing. The dendrimer was reacted with a molar excess of 1,3-propane sultone in acetonitrile.The idea behind the sulfonation was to increase the electrical conductivity of the films.

The second generation dendrimer was sulfonated through the alkanesulfonate process to produce a highly ionic moiety. The sulfonated dendrimer was blended with Nafion to the extent that the calculated equivalent weight of the membrane blend is 640. Membranes were produced by solution casting a blend of sodium-form Nafion and sodium-form sulfonated dendrimer. After casting, the membranes are initialized back into acid-form.

Solvent uptake studies were performed on second generation sulfonated dendrimer/Nafion blends samples for both methanol and water in sodium- and acid-forms. With the addition of the sulfonated second generation dendrimer in low concentration (0.25:1 amine/sulfonate before alkanesulfonation), both the methanol and water uptake increased in both counterion forms. With an increase in the concentration of sulfonated dendrimer, methanol values decreased to slightly above Nafion 117 in the acid-form, and slightly below Nafion 117 in the sodium-form. This trend suggests that higher dendrimer contents should lower the methanol content. As a whole, larger amounts of solvent uptake were found for membranes in the acid-form.

Initial solvent uptake studies of the sulfonated membranes show methanol uptake equal to that of Nafion 1100 and water uptake slightly increased. Solvent uptake studies of methanol and water for the 0.25:1 blends of both the sulfonated and non-sulfonated dendrimer with Nafion have shown values similar to that of Nafion 117, while the 2:1 blend of the non-sulfonated dendrimer with Nafion has uptake values far lower. Solvent uptake studies were performed on blends of Nafion/second generation sulfonated dendrimers in ratios equal to that of the previously tested non-sulfonated dendrimers. The ratios are 0.25:1, 0.5:1, 1:1, 1.5:1, and 2:1 amine groups/sulfonate groups. The sulfonated samples show water uptake values similar to that of Nafion 117, while methanol uptake is slightly higher than Nafion 117, but decreases with an increase in dendrimer concentration.

Sulfonated dendrimer/Nafion membranes with a range of dendrimer concentrations were analyzed by ac impedance. The sulfonated dendrimer/Nafion blends had higher dielectric constants than the

as-received Nafion 117 over a range of frequencies from 5Hz to 13 MHz. Solvent uptake studies have shown that the Na-form blends uptake less methanol and water than the membranes converted back into the acid-form.

AC impedance spectroscopy was used to investigate the effect of addition of dendrimer, sulfonated and non-sulfonated, to Nafion. The addition of the second generation dendrimer in a 2:1 sulfonate/amine ratio yielded a dielectric constant that was higher throughout most of the frequency range (5 Hz- 13 MHz) than for the as-received Nafion 117. Sulfonation of the second generation dendrimer before addition dramatically increased the dielectric constant, providing values higher than Nafion 117 throughout the frequency range. The Cole-Cole plots of the as-received Nafion and sulfonated dendrimer-modified membranes were very different and will be investigated further. Membrane conductivity will be analyzed through ac impedance spectroscopy and dynamic mechanical analysis will be performed to determine the mechanical response of the membranes as a function of temperature.

Blends of Nafion/second generation sulfonated dendrimers in the sodium form were analyzed by wide angle x-ray diffraction (WAXD). Membranes were cast with varying concentrations of sulfonated dendrimer ranging from zero (pure sodium form) to 2:1 ratio of amine/sulfonate groups. WAXD indicates that all Nafion/sulfonated dendrimer blends tested retain crystallinity. Differential scanning calorimetry (DSC) will be used to further investigate any effects that the sulfonated dendrimer may have on the membrane crystallinity.

Differential scanning calorimetry (DSC) was used to investigate thermal transitions in the sodium-form Nafion/sulfonated dendrimer blends before initialization back into the acid-form. Pure sodium-form Nafion shows a thermal transition between 225 and 260°C attributed to the crystalline melting of Nafion. Addition of sulfonated dendrimer reduces the size of the endothermic peak as well as the endothermic peak temperature. The thermal transitions found for the Nafion/sulfonated dendrimer blends were similar to those found previously in the non-sulfonated dendrimer blends.

Sulfonated dendrimer/Nafion membranes with a range of dendrimer concentrations were analyzed by differential scanning calorimetry (DSC). The thermograms indicated that an increase in dendrimer concentration led to a slight decrease in the amount of crystallinity obtained during the casting procedure. Three samples of Nafion/sulfonated poly(propylene imine) dendrimer blends have been sent to IFC for MeOH crossover and PEM analysis.

Fuel cell testing of blends of Nafion and first and second generation dendrimers in the acid-form were performed by IFC. The membrane in the pure form (no dendrimer) exhibited lower resistivity and methanol crossover compared to as-received Nafion 117. Blends of Nafion/second generation dendrimer showed a significant decrease in methanol crossover but the resistance values were somewhat higher than Nafion 117.

One sulfonated and two non-sulfonated second generation dendrimer/Nafion blends have been prepared and sent to IFC for evaluation. The non-sulfonated dendrimer blends were prepared with amine/sulfonate ratios of 0.25:1 and 2:1. The sulfonated dendrimer blend was prepared with the same concentration of dendrimer as in the 0.25:1 non-sulfonated blend but the dendrimer has been alkanesulfonated with 1,3-propane sultone.

The performances of two non-sulfonated second generation dendrimer/Nafion membranes evaluated by IFC were below previous levels. The blends were prepared with amine/sulfonate ratios of 0.25:1 and 2:1. Two more non-sulfonated second generation dendrimer/Nafion membranes have been prepared with more rigorous temperature control during the casting procedure. In addition,

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these membranes have also been mechanically pressed at 180°C. The newly prepared non-sulfonated membranes have been sent to IFC for cell testing. Sulfonated dendrimer/Nafion samples with the same dendrimer concentration as the non-sulfonated form will also be prepared and sent to IFC for evaluation.

In addition, USM prepared PVDF/ Nafion blend membranes. The PVDF composition in the melt-processed membranes ranged from 10 wt% to 60 wt%. Representative membranes were sent to IFC for MeOH crossover and analysis in a PEM fuel cell. Unfortunately, these membranes were too small to test in IFC hardware. Since UCONN is preparing similar materials, it was decided not to evaluate these materials in a fuel cell.

Task II. Advanced Catalysts for Direct Methanol Fuel Cells

This task is divided into three areas: (1) advanced platinum alloy catalysts for cathodes, (2) improved binary and ternary catalysts for the anode, and (3) redox couples for the methanol anode.

Methanol tolerant cathode catalyst development.—In the last quarter we reported on the high oxygen reduction activity of supported alloy catalysts. Because of the high rate of methanol crossover with Nafion 117, low loaded supported alloy catalysts show poor performance in direct methanol fuel cells compared to high loaded platinum black. Consequently, we attempted to prepare an unsupported catalyst for a cathode catalyst, the catalyst was Pt/Rh/Fe black. Supported catalyst of the same material showed improved oxygen reduction performance over platinum in PEM cells. The BET surface area of the black was 82.7 m^2/g. The performance in a direct methanol fuel cell was poor. The iR of the cell was high and increased with time. It was suspected that the Fe may not be stable in the material. Subsequent XRD analysis indicated that in contrast to the supported material, the metal black was not alloyed.

Anode Catalysts – IFC also prepared a platinum palladium anode catalyst. This catalyst has shown promise as a CO tolerant catalyst. The surface are of the Pt/Pd by BET was 39 m^2/g. The performance of the material is shown below in Figure 1. It's performance is poor. XRD analysis of the Pt/Pd catalyst indicated that this material was a mixture of PdO and Pt and not an alloy.

Redox Couple Catalysts – The approach being taken by UCONN in this task involves the incorporation of redox catalysts on the anode catalyst carbon support to facilitate the oxidation of the carbon monoxide that is considered to be a poisoning intermediate for the direct oxidation of methanol on platinum catalyst. The catalysts, consisting of platinum with ruthenium tetramethylcyclam(14) supported on heat-treated Vulcan XC-72 and platinum with ruthenium tetramethylcyclam(15) supported on heat-treated Vulcan XC-72, were previously reported to result in higher catalytic activity than platinum alone on the basis of current per unit platinum surface area at a given polarization. Potentiometric evaluation of these two catalysts shows that a reversible redox potential was lowered from 0.43 to 0.35 volts by the change from cyclam(14) to (15) in the direction anticipated. The number of active sites on the cyclam indicate that the turnover number on the affected platinum sites is very high. Since the cyclam(14) already has an activity about half of platinum/ruthenium on the basis of current per unit of platinum area, an increase in the number of the active sites would lead to a good catalyst. Attempts are planned to increase the number of active sites by reducing the percentage of platinum on the carbon support and modifying the tethering of the macrocyclic to the support.
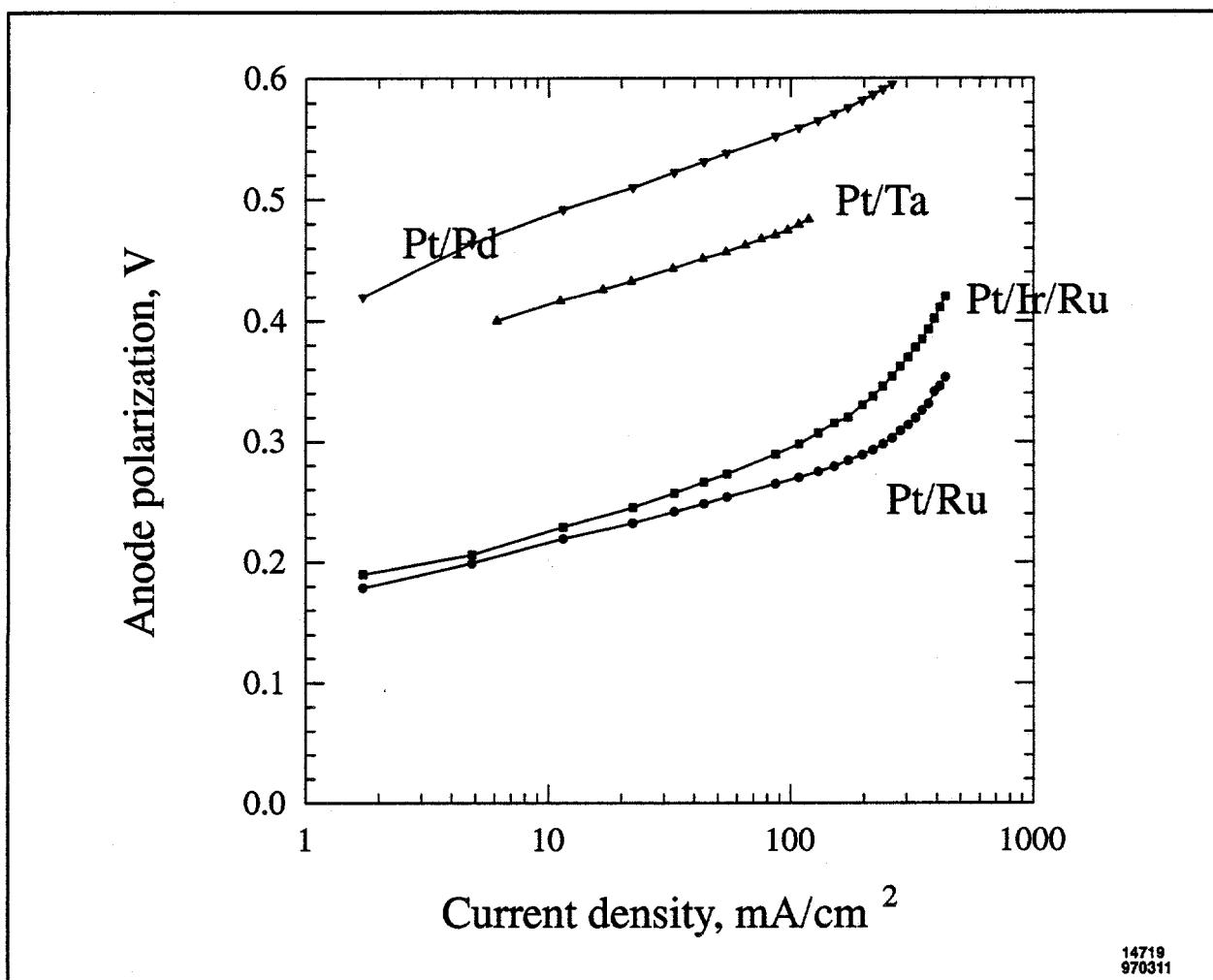
Figure 1. Anode Polarization (iR Compensated) Data For Pt/Pd And Other Anode Catalysts.

Because of the enhanced activity for direct methanol oxidation measured with the catalyst consisting of platinum with ruthenium tetramethylcyclam(15) supported on heat-treated Vulcan XC-72 compared to a similar catalyst using ruthenium tetramethylcyclam(14), another similar catalyst was prepared using ruthenium tetramethylcyclam(16). This cyclam was expected to give an even lower redox potential than the (15). This catalyst showed poorer activity than both the (14) and (15) and a redox potential that had not been reduced.

A catalyst containing a lower percentage of platinum on a graphitic carbon support is being prepared to increase the ratio of macrocyclic compound to platinum to enhance the beneficial effect of the macrocyclic. The catalytic activity of a porphyrin in the absence of the central metal is being evaluated to determine the importance of that metal on the beneficial effect of the macrocyclic. A catalyst containing a 2% platinum on the heat-treated carbon support was prepared to increase the ratio of macrocyclic compound to platinum to enhance the beneficial effect of the macrocyclic. No beneficial effect was found because of a large platinum crystallite size. This approach will be repeated. An increase of the content of cyclam(15) on 15% platinum on the heat-treated carbon support was found to significantly increase the activity above that of the catalyst without the cyclam(15) on a mA/mg Pt basis.

This cyclam is currently being evaluated. A voltammetric study is being conducted to determine the significance of the ruthenium central metal on the redox characteristics of a porphyrin. In the absence of the ruthenium, the material retains similar but less reversible redox characteristics. Additional tests are needed to eliminate the possibility that a trace metal from the Vulcan XC-72 support is contributing to the redox properties.

Figure 2 compares the anode polarization of cmmercial PtRu/C catalyst. Although better than Pt, the activity of RuTMC15 is not as good as Pt/Ru.

Task III. Direct Methanol Fuel Cell Testing

Membrane and catalyst evaluation has continued in accordance with the protocol established in previous reports. Results of these tests have been included under the appropriate tasks for continuity purposes.

Task IV. Performance Analysis and Conceptual Design

Comparison with a Hydrogen Fueled System – Figure 3 compares a direct methanol and a H_2-air fuel cell systems. For this example, the weight of the system includes the fuel and storage vessel for three hours of operation at rated power. The hydrogen power plant is based on the prototype FORD PEM power plant that IFC constructed under DOE contract DE-AC02-94CE50389. For the direct methanol fuel cell system, the specific power (W/kg) is plotted as a functions of system efficiency for different cell stack performances. Here the efficiency is calculated based on the lower heating value of the fuel. These options include the system based on demonstrated stack operational characteristics, and others incorporating developmental goals including: (1) higher air utilization's, (2) lower methanol crossover in the fuel cell stack, and (3) improvements in the cell stack performance. For the hydrogen system, the efficiency of the power plant is assumed constant and the specific power varies with the assumed density of H_2 storage, from 1 to 10 wt%. This represents H_2 storage technologies ranging from conventional pressurized steel tanks (less than 1 wt%), to commercially available fiberglass wrapped composite tanks (~5 wt%), to super advanced composite tanks (~10 wt% or more). The figure shows that, although the direct methanol systems are less efficient, they are weight competitive with H_2-air power plants with 1 to 5 wt% H_2 storage.
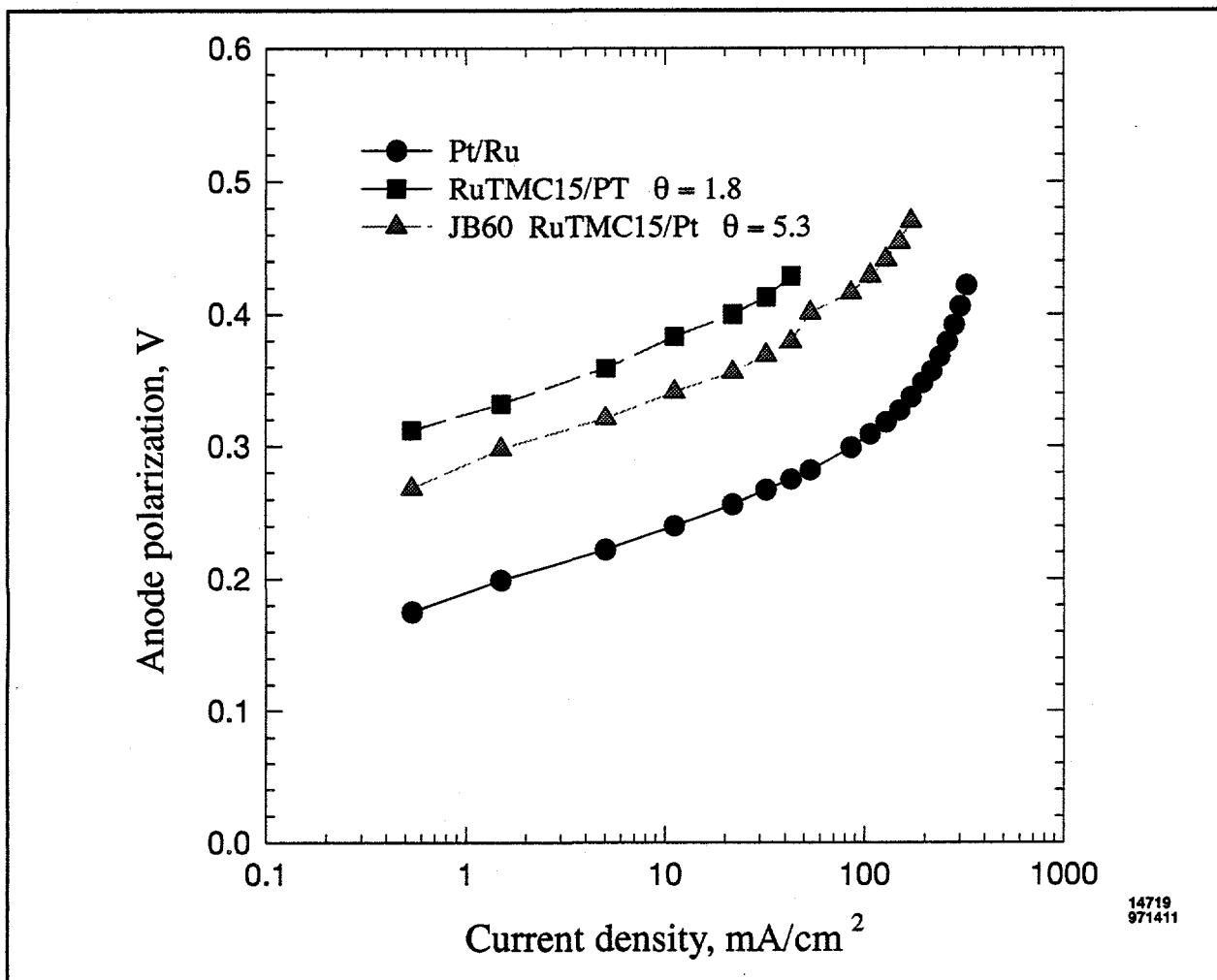
Figure 2. Anode Polarization (iR Compensated) For Redox Couple And Pt/Ru Catalysts.
Loadings For All Electrodes Was 1 mg Pt/cm².

The system weights used to generate this figure are for a 50 kW transportation power plant, including all the system components necessary for stand alone operation including sufficient fuel for three hours at full rated power. Figure 3 shows the impact of several potential improvements to the baseline DMFC fuel cell system that would make it competitive in weight to the H_2-air PEM power plant. The improvements and their impact on system weights include : (1) reduced methanol crossover, (2) higher utilization of air, and (3) improved cell performance.

Decreased Methanol Crossover: Dropping the base line condition of 194 mA/cm² equivalent methanol crossover to 65 mA/cm² crossover lowers the total weight of a 50 kW system from 1031 kg to 825 kg. Less methanol crossover lowers fuel consumption and lowers process air consumption with its associated parasite power. The net effect is higher system efficiency and lower gross power output, which lowers fuel storage requirements, reduces cell stack size, and results in a lower weight thermal management system.

Higher Air Utilization's in the Cell Stack: Raising air utilization's from 25 to 50% has similar impact on system weights dropping the base line system weight from 1031 kg to 872 kg. Again the system is more efficient because less process air is required. This lowers fuel storage requirements, reduces cell stack size, and decreases the weight of the thermal management system. The improve-

ments of lower crossover and higher air utilization's could be combined to lower overall system weights even more. Because the system is at ambient pressure, the parasite power is relatively low. Not explicitly shown in this figure is the impact of reduced air flow on water and thermal management.

Improved cell performance: Higher cell performance permits operation at higher cell voltages improving the system efficiency, and it also raises cell operating power densities resulting in smaller fuel cell stacks. Raising the cell performance from the baseline condition (0.36 V/cell @ 200 mA/cm^2) to 0.5 V/cell at 350 mA/cm^2 lowers the 50 kW DMFC system weight from 824 kg to 368 kg. These cell performance parametric studies also assumed a decrease in methanol crossover from 194 mA/cm^2 to 65 mA/cm^2 but no change in the baseline 25% air utilization. The 368 kg system results in a net specific power of 136 W/kg. The same specific power H_2-air PEM fuel cell system operates at high performance (0.6 V/cell at 645 mA/cm^2) and has a 5 wt% hydrogen storage sub-system. This is an expensive, relatively advanced gas tankage option consisting of graphite epoxy composite tankage pressurized to at least 20.7 M Pa (3000 psig). Therefore an advanced DMFC fuel cell system could be weight competitive with an advanced H_2-air PEM fuel cell system.
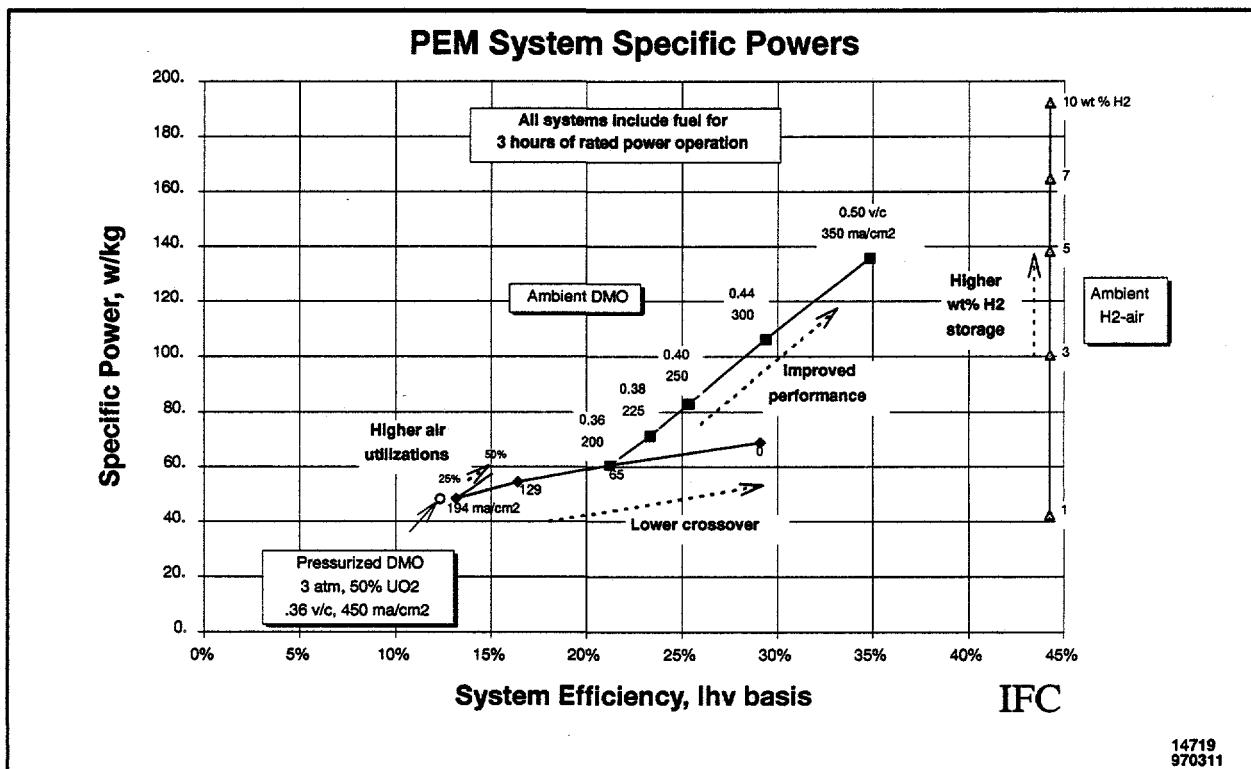

Figure 3. Specific Power And System Efficiency.

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Baseline Systems Weight Comparison: H$_2$-air and DMFC

Each DMFC system option was computer modeled to determine its efficiency, thermal, and fluid flow characteristics, information necessary to estimate the weights of system components including the fuel storage system. Thermodynamic data for the H$_2$-air system was calculated or taken from system models. The following Table 2 summarizes key thermodynamic factors for each system including those used in scaling component sizes from the H$_2$-air system to the DMFC system.

Table 2. Summarized Key Thermodynamic Factors		
	PEM H2-Air	**Direct Methanol Oxidation (DMO)**
Gross DC power	52.5 kW	62.4 kW
Net DC power	50.0 kw	50.0 kw
System efficiency (LHV)	44%	13%
Process air flow	473 kg/hr	1750 kg/hr
Process fuel flow	3.4 kg/hr H2	50.5 lbs/hr pure Methanol
Radiator heat rejection	62.7 kW	314 kW
Air Utilization	28%	25%
Overall Fuel Utilization	98%	99%
Effective Fuel Utilization	98%	50%
Cell rated power operation:		
volts per cell	0.60	0.36
mA/cm^2	600	200
crossover mA/cm^2	0	194

For the 'base line' H$_2$-air and DMFC cases the following system weight comparison was derived. The H$_2$-air case weights are for the most part based on components designed and specified for the 50 kW Ford automotive power plant while the DMFC system components weights are scaled from the Ford weights by the appropriate factors derived from the computer models.

The fuel storage system assumes 150 kW-h capacity, enough fuel to run at rated power for three hours. For the baseline DMFC system this consists of 206 kg of neat ('pure') methanol. No weight allocation was included for the methanol fuel tank because it is low pressure, most likely plastic construction, and very light relative to the bulk fuel weight. On the other hand the weight of H$_2$ storage system is mostly tankage. The baseline H$_2$-air system shown in Table 3 assumed the use of modern composite tankage. These tanks have an aluminum liner wrapped with epoxy-glass fibers and they are pressurized to 20.7 M Pa (3000 psig). The tanks are capable of about 3 wt% H$_2$ storage, and in the baseline 50 kW H$_2$-air system the 10.2 kg of H$_2$ gas needed for 150 kW-h of operation requires a tank weighing 340 kg.

Table 3. 50 kW Baseline System Component Weights, kg		
	Ford H$_2$-Air	DMFC
Power Section Subsystem (PSS)	99.5	630
Thermal Management System (TMS)	28.6	158
Air Processing System (APS)	13.2	20.9
Electrical Control System (ECS)	14.5	14.5
Fuel Processing System (FPS)	2.7	2.7
Fuel Storage (150 kWh storage)	340	206
Total System Weight , kg	498	1031
System specific power , W/kg	100	49

Scaling factors for estimation of DMFC system weights

The DMFC system component weights shown in Table 4 were scaled from similar components defined for the 50 kW Ford H$_2$-air PEM power plant. Scaling factors and other key assumptions used to determine the DMFC component weights include:

Table 4. DMFC System Component Weights		
	Ford H$_2$-Air	**DMFC**
<u>Stack Repeat Parts:</u>	<u>5.9 kg/m^2 active area</u>	<u>5.9 kg/m^2 active area</u>
Relevant system data:	0.60 @ 646 mA/cm^2	0.36 v/c @ 200 mA/cm^2
Equivalent crossover	none	200 mA/cm^2
Gross power	52.5 kW	62.4 kW
	13.6 m^2 active area	86.8 m^2 active area
Total component weight:	80.5 kg	514 kg
<u>Stack Non-Repeats:</u>	<u>9.6 kg/stack</u>	<u>9.6 kg/stack</u>
Relevant system data:	~ 200 cells/stack	200 cells/stack
	2 stacks for 50 kw	12 stacks for 50 kw
Total component weight:	19.2 kg	116 kg
<u>Air Processing System</u>	<u>ratio by relative blower kW</u>	
Relevant system data:	air blower: 2.0 kW	air blower: 3.2 kW
Total component weight:	air blower: 4.5 kg	7.2 kg
Total component weights:	blower BOP: 8.6 kg	14.6 kg
<u>Radiator</u>	<u>ratio by relative radiator duty</u>	
Relevant system data:	62.7 kW	314 kW
Total component weight:	~ 18.2 kg (estimated)	90 kg
<u>Radiator Fan & Motor</u>	<u>ratio kw by relative radiator duty</u>	
	<u>2.3 kg/kW (fan + motor) weight</u>	
Relevant system data:	1.73 kW motor	8.67 kW motor
	72% eff. fan	72% eff. fan
Total component weight	:~ 4.1 kg	47.1 kg
<u>Balance of TMS</u>	<u>ratio by relative radiator duty</u>	
Total component weight:	9.4 kg	47.1 kg
<u>Fuel System BOP</u>	2.7 kg	2.7 kg
<u>Electrical Control System</u>	14 kg	14 kg

Task V. Demonstration Plan

No work was scheduled or accomplished on this task during the period covered by the report.

Section III Current Problems

Task I. Development of Methanol Impermeable Membranes

The results for methanol permeability measured in the fuel cell are higher than those measured in out of cell tests. Further, reproducibility of methanol crossover and resistance needs to be improved, particularly with the dendrimer membranes.

Task II. Advanced Catalysts for Direct Methanol Fuel Cells

Supported Alloy Catalysts – Although the supported catalysts have shown superior oxygen reduction activity in half cell and H_2/air PEM cells, loadings are limited to about 1 mg Pt/cm^2. Therefore, the performance of low loaded Pt alloy catalysts is not as good as high loaded (5 mg Pt/cm^2) platinum black electrodes.

Section IV Work Planned

Task I. Development of Methanol Impermeable Membranes

The focus for most of the work in the next quarter will be to reproduce the promising results obtained thus far. We will also identify the best membranes for fabrication of a combined MEA.

Task III. Direct Methanol Fuel Cell Testing

Testing of membrane samples from USM, University of Iowa, and UCONN will continue. The redox couple catalyst will also be evaluated. We will also work to improve the performance of MEA's made with supported alloy catalysts. When this is completed, a MEA with the best available anode catalyst, cathode catalyst, and membrane will be made.

Task IV. Performance Analysis and Conceptual Design

Minor changes to the systems analysis presented here are planned for the next quarter.

Task V. Demonstration Plan

In June a review meeting with DOE was held at IFC. At this time J. Milliken indicated that because of budgetary constraints, follow on funding was not available. In light of the promising results being obtained with the methanol impermeable membrane task, it was agreed that no work would be executed under task 5 and the funds would be used to continue testing and evaluation of membranes.

Section V Schedule Status

DIRECT METHANOL FUEL CELLS FOR TRANSPORTATION APPLICATIONS

ID	Task Name
1	Task 1.CH3OH Imp. Membrane
2	Retain Nafion in matrix
3	Crosslinked membrane
4	intial UCONN samples
5	Dendrimer modified membrane
6	initial S. Miss. sample
7	low crossover membrane established
8	Task 2. Advanced Catalyst
9	Cathode catalysts
10	Pt-Co-Cr & Pt-Ir-Cr catalysts
11	catalyst characterization
12	cathode catalyst est
13	Redox couple
14	initial redox samples
15	Anode catalysts
16	Pt/Ru catalyst
17	Pt-Ta &Pt-Ir-Ru catalyst
18	catalyst characterization
19	half cell evaluation
20	anode catalyst est.
21	Task 3. DMFC Testing
22	test stand preps
23	establish baseline
24	anode MEA
25	cathode MEA
26	U. S. Miss. membrane
27	UCONN membrane
28	redox couple
29	single cell demonstrated
30	Task 4. Perf. Anal. & Design
31	design criteria

Quarters / Months header:
er | 3rd Quarter (Jun Jul Aug Sep) | 4th Quarter (Oct Nov Dec) | 1st Quarter (Jan Feb Mar Apr) | 2nd Quarter (May Jun) | 3rd Quarter (Jul Aug Sep) | 4th Quarter (Oct Nov Dec)

Legend:
Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone ◇
Rolled Up Progress

Project: DOE DMO Program
April 3, 1997

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DIRECT METHANOL FUEL CELLS FOR TRANSPORTATION APPLICATIONS

ID	Task Name
32	conceptual design
33	design concept completed
34	**Task 5. Demonstration Plan**
35	Phase II plan
36	Phase II plan accepted
37	**Task 6. Management and Reporting**
38	monthly and quarterly
39	Final report

Column headers (time scale): 3rd Quarter (Jun, Jul, Aug, Sep) | 4th Quarter (Oct, Nov, Dec) | 1st Quarter (Jan, Feb, Mar) | 2nd Quarter (Apr, May, Jun) | 3rd Quarter (Jul, Aug, Sep) | 4th Quarter (Oct, Nov, Dec)

Legend:
- Task
- Progress
- Milestone
- Summary
- Rolled Up Task
- Rolled Up Milestone ◇
- Rolled Up Progress

Project: DOE DMO Program
April 3, 1997

Cost Performance Report

DOE F1332.12
(11-84)

FORM APPROVED
OMB 1901-1400

U.S. DEPARTMENT OF ENERGY
COST PERFORMANCE REPORT - WORK BREAKDOWN STRUCTURE

Field	Value
1. TITLE	ADVANCED FUEL CELLS FOR TRANSPORTATION APPLICATION
2. REPORTING PERIOD	June 1997
3. IDENTIFICATION NUMBER	DE-AC08-96NV11984
4. PARTICIPANT NAME AND ADDRESS	International Fuel Cells, 195 Governors Highway, South Windsor, CT 06074
5. COST PLAN DATE	07/05/96
6. START DATE	May 28, 1996
7. COMPLETION DATE	June 30, 1997
8. NEGOTIATED COST	$729,283
9. ESTIMATED COST OF AUTHORIZED UNPRICED WORK	$0
10. TARGET PROFIT/FEE %	0%
11. TARGET PRICE	$729,283
12. ESTIMATED PRICE	$729,283
13. SHARE RATIO	71/29
14. CONTRACT CEILING	$729,283
15. ESTIMATED CEILING	$729,283

16. WBS ELEMENT	CURRENT PERIOD					CUMULATIVE TO DATE					AT COMPLETION		
	BUDGETED COST		Actual Cost of Work Performed	VARIANCE		BUDGETED COST		Actual Cost of Work Performed	VARIANCE		Budgeted	Revised Estimate	Variance
	Work Scheduled	Work Performed		Schedule	Cost	Work Scheduled	Work Performed		Schedule	Cost			
TASK 1	18	18	3	0	15	203	203	163	0	40	222	222	0
TASK 2	12	12	2	0	10	185	185	169	0	16	197	197	0
TASK 3	0	0	18	0	-18	61	61	83	0	-22	61	119	-58
TASK 4	0	0	13	0	-13	30	30	52	0	-22	30	65	-35
TASK 5	0	0	0	0	0	39	39	0	0	39	39	0	39
TASK 6	1	1	7	0	-6	62	62	47	0	15	62	58	4
17. WBS TOTAL	31	31	43	0	-12	580	580	514	0	66	611	661	-50
18. COST OF MONEY	0	0	0	0	0	0	0	0	0	0	0	0	0
19. GENERAL & ADMIN	6	6	4	0	2	112	112	53	0	59	118	68	50
20. UNDIST. BUDGET													
21. SUBTOTAL	37	37	47	0	-10	692	692	567	0	125	729	729	0
22. SHARE	25	25	0	0	25	296	296	296	0	0	296	296	0
23. TOTAL	62	62	47	0	15	988	988	863	0	125	1025	1025	0

RECONCILLIATION TO CONTRACT BASE

24. VARIANCE ADJMNT	0	0
25. TOT. CONTRACT VAR	0	0

26. DOLLARS EXPRESSED IN: Thousands

27. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER

28. DATE: 7/14/97

Variance Analysis

The cost of Task 3, Cell Testing, is larger than planned. It is anticipated that this will continue next quarter, as many more samples of membranes are expected to be received for testing from the sub-contractors. As mentioned earlier, no work is scheduled for Task 5, and therefore this will continue to show up as a positive variance. The cost of Task 4 is above the planned level, this represented the detailed system analysis reported here.