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EXECUTIVE SUMMARY

The overall goal of this program is development of an advanced proton-exchange membrane (PEM) for use as the electrolyte in a liquid feed direct methanol fuel cell (LFDMFC), which provides reduced methanol crossover, while simultaneously providing high conductivity and low membrane water content. To develop this advanced membrane, a team consisting of Giner, Inc. and BetaCure Technologies, Inc. (BCT) was put together. The primary role of BCT was to fabricate membranes to Giner, Inc.'s specifications. Giner, Inc. directed the overall effort, evaluated the advanced membranes in bench-top testing, fabricated membrane-electrode assemblies (MEAs) and ultimately demonstrated feasibility of the advanced membrane in a multi-cell LFDMFC stack.

Our approach to develop a low-cost, high-methanol exclusion PEM for use in a DMFC was based on use of a membrane containing precross-linked fluorinated base polymer films and subsequently grafting the base film with select materials. The technique used for grafting was developed by BCT and involved the use of beta and/or gamma radiation. Films were then sulfonated to provide proton conductivity.

During this Phase I program, BCT prepared over 80 different membranes. These membranes were prepared by irradiating a base film with up to 70Mrad of radiation, soaking the irradiated film in a mixture of styrene, divinyl benzene and triallylcyanurate [DVB-TAC] to effect crosslinking within the film, and finally sulfonating and hydrolyzing the film to provide proton conductivity. The purpose of the irradiation of the fluorocarbon base films was to produce free radicals for subsequent grafting and/or to promote pre-crosslinking of the base film to increase tortuosity to reduce methanol permeation. Subsequent to film preparation, they were extensively characterized using standard Giner, Inc. techniques with respect to physical/chemical properties such as ion-exchange capacity (IEC), water content, thickness, dimensional area change, and specific resistivity (ionic conductivity). Films exhibiting acceptable ionic conductivities were fabricated into complete membrane-electrode assemblies and evaluated using typical DMFC conditions (1M methanol/water, 60°C, atmospheric pressure air) for fuel cell performance and methanol permeability.

Using these techniques, the rate of methanol crossover through the advanced membranes was reduced 90% (66% reduction compared to that obtained with Nafion 117). These membranes also exhibited high fuel cell performance i.e. within 90% or higher than that obtained with Nafion 117. A 5-cell LFDMFC stack using advanced membrane provided stable performance over a 100-hour life test. Preliminary cost estimates predict a manufacturing cost of the advanced membrane at \$4 to \$9 per kW. Thus, all program objectives were met and feasibility of the concept demonstrated.

1.0 INTRODUCTION

1.1 Purpose of Research

A liquid feed direct methanol fuel cell (LFDMFC) is a potentially attractive power source for electric vehicles (EVs) and other low- to medium-power applications such as uninterruptable power supplies and lawn mowers, in the commercial as well as the military sectors. A significant advantage over indirect methanol proton-exchange membrane fuel cells (PEMFCs) (ones that require a reformer) is that the LFDMFC eliminates the need for an external reformer, reducing system weight, complexity and cost. Benefits to be derived from use of LFDMFCs as power sources compared to current internal combustion engines include dramatic reductions in emissions of air pollutants, reduction in the nation's dependence on imported petroleum (methanol can be made from indigenous fuels such as coal and natural gas, and also from renewable sources such as wood and biomass), and an overall increase in vehicle energy efficiency. Use of liquid methanol fuel avoids the difficulties and hazards associated with the handling of gaseous reactants such as hydrogen. Vehicles powered by LFDMFCs have the potential for a very large market in California, the New England states, and other states in the Northeast that have mandated the introduction of zero-emission vehicles (ZEVs) early in the next century.

One drawback to direct methanol proton-exchange membrane fuel cells (DMPEMFCs) (both liquid and gaseous feed) is that methanol diffusion through currently available proton-exchange membrane (PEM) electrolytes such as Nafion[®] is too large (approximately 10^{-2} cm³/sec), resulting in a loss of approximately 30% of the methanol in the anode feed. Methanol permeates from the anode chamber of the DMPEMFC across the membrane, adsorbs on the cathode catalyst, and reacts with air (O₂), resulting in a parasitic loss of methanol fuel and reduced fuel cell voltage. Performance losses of 40-70 mV at a given current density have been observed at the cathode of PEMFCs with a direct methanol feed (Potje-Kamloth et al., 1992). Küver et al. (1994) have observed a loss of at least 100 mV for the oxygen electrode when operated as a gas-feed DMPEMFC. This translates into an approximately 10% decrease in PEMFC air (O₂) cathode performance output as compared to a cell operating without direct methanol feed. Also, air (O₂) cathode mass transport concerns are aggravated due to wetting of the electrode structure, limiting high current density operation and life. In their development of a PBI/phosphoric acid DMFC, Savinell has reported a methanol crossover rate 10% of that observed with Nafion (Savinell et al., 1994). A drawback to this system, however, is the 150 to 190°C fuel cell operating temperature, which may be too high (long startup time) for the rapid start up required for automotive use.

More recently, Yen has described the use of cross-linked and sulfonated PEEK and PES membranes for DMFC use. However, no crossover or fuel cell performance data was provided (Yen et al., 1998). Pivovar examined the use of pervaporation membranes for DMFC use. In a study based on ionic conductivity (membranes imbibed with H₂SO₄) and methanol permeability (bare membranes), the conclusion was that pervaporation membranes are much better methanol barriers than Nafion. However, their selectivity is often equal to that of Nafion so they are no better when both methanol transport and proton conduction are involved. Instead, it is better to use a membrane that is methanol impermeable and conducts protons without electroosmotic

drag, such as PBI (Pivovar et al., 1999). Taylor and Moore (1998) fabricated recast Nafion membranes containing poly(propylene imine) dendrimers to inhibit methanol crossover. In complete DMFC testing, they observed up to a 35% reduction in crossover compared to baseline Nafion performance.

Researchers at LANL have measured a methanol concentration of 0.24M in a Nafion 112 membrane, and have measured a methanol diffusion coefficient through a Nafion membrane of $1.13 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Wilson et al., 1995). This diffusion coefficient is in excellent agreement with the value of $1.15 \times 10^{-5} \text{ cm}^2/\text{sec}$ calculated by Verbrugge (Verbrugge, 1989). Skou et al. have found that Nafion membranes in their protonic form and completely solvent saturated behave similarly toward methanol and water, i.e., the membrane does not prefer one to the other. The solvation of the protonic groups are identical for each solvent, 23 molecules per proton (Skou et al., 1997). Obviously, a need exists for membranes with reduced methanol permeability.

The overall goal of this program is to develop an advanced membrane for use as the electrolyte in a LFDMFC, which provides reduced methanol crossover, while simultaneously providing high conductivity and low membrane water content. To develop this advanced membrane, a team consisting of Giner, Inc. and BetaCure Technologies, Inc. (BCT) was put together. The primary role of BCT was to fabricate membranes to Giner, Inc.'s specifications. Giner, Inc. directed the overall effort, evaluated the advanced membranes in bench-top testing, fabricated membrane-electrode assemblies (MEAs) and ultimately demonstrated feasibility of the advanced membrane in a multi-cell LFDMFC stack.

Our approach to develop a low-cost, high-methanol exclusion PEM for use in a DMFC was based on use of a membrane containing precross-linked fluorinated base polymer films and subsequently grafting the base film with select materials. The technique used for grafting was developed by BCT and involved the use of beta and/or gamma radiation. Films were then sulfonated to provide proton conductivity.

During this Phase I program, BCT prepared over 80 different membranes. These membranes were prepared by irradiating a base film with up to 70Mrad of radiation, soaking the irradiated film in a mixture of styrene, divinyl benzene and triallylcyanurate [DVB-TAC] to effect crosslinking within the film, and finally sulfonating and hydrolyzing the film to provide proton conductivity. The purpose of the irradiation of the fluorocarbon base films was to produce free radicals for subsequent grafting and/or to promote pre-crosslinking of the base film to increase tortuosity to reduce methanol permeation. Subsequent to film preparation, they were extensively characterized using standard Giner, Inc. techniques with respect to physical/chemical properties such as ion-exchange capacity (IEC), water content, thickness, dimensional area change, and specific resistivity (ionic conductivity [IC]). Films exhibiting acceptable ionic conductivities were fabricated into complete MEAs and evaluated using typical DMFC conditions (1M methanol/water, 60°C, atmospheric pressure air) for fuel cell performance and methanol permeability.

Using these techniques, the rate of methanol crossover through the advanced membranes was reduced 90% (66% reduction compared to that obtained with Nafion 117).

These membranes also exhibited high fuel cell performance i.e. within 90% or higher than that obtained with Nafion 117.

2.0 TECHNICAL OBJECTIVES

The overall objective of the proposed program was development of an advanced PEM, which will be used as the electrolyte in LFDMFC systems. The LFDMFC will be used as the power source in an electric vehicle. Design goals of the advanced membrane included an area-specific resistance of less than 0.2 ohm-cm^2 and little or no diffusion of methanol across the membrane.

The goal of this Phase I program was to demonstrate operation of the advanced membrane in a complete LFDMFC stack. Specific objectives to accomplish this goal included the following:

- To demonstrate feasibility of fabricating a low-resistance high-methanol-exclusion membrane for use in a LFDMFC.
- To evaluate select, important physical/chemical properties of the advanced membrane.
- To demonstrate performance of the advanced membrane initially in single-cell testing followed by operation of a multi-cell LFDMFC stack.
- To conduct a cost analysis, projecting the manufacturing cost of the advanced membrane and associated MEAs in large quantities.

Specific Questions to be answered during the course of the program included:

- Could the proper conditions required to fabricate a high-exclusion membrane be identified?
- Could the membrane provide the required characteristics of low resistance, high methanol exclusion, and good mechanical strength?
- Would a fuel cell fabricated with the advanced membrane provide DMFC performance at least comparable to that presently obtainable with Nafion and, if not, what performance level would be required to provide competitive fuel cell performance?
- Can MEAs fabricated using the advanced membrane approach DOE's cost goal of \$10/kW?

During this Phase I CARAT program we have made significant progress in demonstrating the feasibility of this proposed concept by fabricating a proton-exchange membrane that exhibits high fuel cell performance and low methanol permeability. The best

membrane prepared to date has a low specific resistivity of 0.2 to 0.3 $\Omega\text{-cm}^2$ and reduced methanol permeation through the membrane by 90%. This is a reduction of 66% compared to Nafion 117. The membranes have high tensile strength and are very flexible. Performance of these membranes is within 90% or higher than that of Nafion 117 during operation in a DMFC.

3.0 DEGREE TO WHICH PHASE I TECHNICAL OBJECTIVES HAVE BEEN MET

The specific objectives of the Phase I CARAT program were summarized above; the degree to which these objectives were met, are summarized below, followed by specific details of the work performed during Phase I.

To demonstrate feasibility of fabricating a low-resistance high-methanol-exclusion membrane for use in a LFDMFC: Membrane fabrication conditions were identified resulting in a proton-exchange membrane that reduced methanol crossover ($\geq 90\%$ exclusion). This was a reduction in methanol crossover of 66% as compared to baseline Nafion 117 membrane, while simultaneously providing high fuel cell performance. This objective was fully met.

To evaluate select, important physical/chemical properties of the advanced membrane: All membranes were extensively characterized with respect to their physical/chemical properties and correlated to their method of manufacture and cell performance. This objective was fully met.

To demonstrate performance of the advanced membrane initially in single-cell testing, followed by operation of a multi-cell LFDMFC stack: Membranes exhibiting acceptable resistance values were evaluated in complete LFDMFCs. The best membrane evaluated to date provided DMFC performance comparable to that obtained using Nafion while simultaneously providing over a 66% reduction in methanol crossover. The multi-cell stack was run for 100 hours. This objective has been fully met.

To conduct a cost analysis, projecting the manufacturing cost of the advanced membrane and associated membrane-electrode assemblies (MEAs) in large quantities: A preliminary cost analysis has shown that the estimated cost for the membrane is \$11 to \$21/ m^2 (\$1 to \$2/ ft^2) or \$4 to \$9/kW. This objective has been fully met.

4.0 PHASE I RESULTS

4.1 Research Findings and Results

4.1.1 Membrane Preparation and Evaluation

During this program a total of over 80 films were fabricated by BCT and evaluated by Giner, Inc. (See appendix A for a complete listing of the films fabricated and evaluated during this program. These materials were prepared using systematic variations in processing parameters to determine their effect on overall membrane properties.) Due to the large number of films that were tested only those films along with the processing conditions that led to the development of an advanced membrane possessing properties of low methanol

permeation and low film resistance will be discussed here; these materials have been listed in Table 1. Discussion of additional materials tested has been relegated to Appendix A.

Table 1. Typical Candidate Advanced Membranes

Film Sample ID	Base Cross-linking Radiation (Mrad)	Monomer Graft (% Styrene)	Cross-Linking Agent* (% DVB)	Grafting Period (Hours)	% Weight Gain
s588-06-01	2	10	1	24	1.4
s588-07-01	2	25	1	27	0.7
s588-07-02*	2	50	1	27	25.8
s588-08-01	2	75	1	27	89.0
s588-11-01*	2				
s588-11-02*	2	50	1	21.5	23.8
s588-11-03	2	50	1	25	28.3
s588-12-01	2	50	1	5.75	5.5
s588-12-02	2	50	1	8	8.2
s588-12-03*	2	50	1	15	16.6

4.1.2 Test Results

Subsequent to preparation, films were extensively characterized using standard Giner, Inc. techniques with respect to physical/chemical properties such as ion-exchange capacity (IEC), water content, thickness, dimensional area change, and specific resistivity (ionic conductivity). Films exhibiting acceptable ionic conductivity were fabricated into complete MEAs and evaluated using typical DMFC conditions (1M methanol/water, 60°C, atmospheric pressure air) for fuel cell performance and methanol permeability.

Membrane development in this Phase I project was based on an iterative process, in which membranes were prepared, evaluated, and then modified, based on test results. During the program we discovered that it was possible to fabricate a membrane with a low resistance, high ion exchange capacity, and DMFC performance equivalent to that of Nafion 117. Water contents of early films were three times higher than that of the baseline Nafion membrane. It was observed that the high water content of grafted fluorocarbon membranes was associated with a high methanol permeability rate. To further reduce methanol permeability, the selection of membranes in Table 1 was chosen based on their low water content. The advanced membranes exhibited water contents in the range of 30 to 40% with IECs above that of Nafion 117.

All films exhibited high tensile strength in the hydrated and dehydrated states with respect to the baseline film. Due to low graft percent, several of the films exhibited resistances above 1.0 $\Omega\text{-cm}^2$ (Table 2) and were eliminated from further testing.

Table 2. Membrane Specific Resistivity

Film Sample ID	Specific Resistivity* (H⁺) (Ω-cm²)
S588-06-01	1.000+
S588-07-01	1.000+
S588-07-02*	0.282
S588-08-01	0.110
S588-11-01*	0.305
S588-11-02*	0.160
S588-11-03	0.290
S588-12-01	1.000+
S588-12-02	1.000+
S588-12-03*	0.300
Nafion [®] 117 (Baseline)	0.150 - 0.229

* Contact Pressure = 500 psi, films in H⁺ form with Pt black bonded electrodes

4.1.3 Direct Methanol Fuel Cell Testing

Select films were chosen for DMFC testing. The selection was based more heavily upon water content and specific resistivity of the membrane. The surface of the experimental films remained flat and suitable for electrode attachment. Electrode structures were thermally bonded to the membrane samples and tested in the DMFC under standard operating conditions of 1M methanol/water as the anode feed, air at atmospheric pressure as the cathode feed, and an operating temperature of 60°C. The membranes were fabricated into MEAs using Giner, Inc. Pt-Ru anode and Pt black cathode electrode structures (4 mg/cm² loadings of each). The MEAs were placed in DMFC hardware (25-cm² active area) and performance data collected during fuel cell operation. MEAs tested in the DMFC were also evaluated for methanol permeability. Permeability measurements were obtained at open circuit voltage (no load) and at a current density of 100 mA/cm² by measuring the quantity of CO₂ in the cathode effluent gas. Several baseline MEAs fabricated with Nafion 117 membrane were also tested for comparison. It was discovered that variations in electrode processing/fabrication could lead to variations in methanol permeation through the same membrane. Therefore a baseline MEA (Giner No. 554-68-0) fabricated with Nafion 117 using the exact same electrode structures (including catalyst loading, binder/ionomer content, pressing conditions, etc.) was chosen as a direct comparison to membranes developed during this Phase I project when obtaining crossover measurements.

Although several base films were investigated, only select base film grafted and crosslinked with styrene/DVB exhibited high methanol exclusion characteristics. MEAs were fabricated from film samples s588 - (07-02, 11-01, 11-02, and 12-03) placed in DMFC hardware and performance data collected during fuel cell operation. Test results obtained with Nafion 117, tested in the same fuel cell hardware under similar operating conditions, are included as a baseline comparison. A summary of the completed fuel cell testing is listed in Table 3 and shown graphically in Figure 1.

Figure 1. DMFC Performance of Low-Graft Membranes

Table 3. Summary of Direct Methanol Fuel Cell Testing

Film Sample ID	MEA#	CH ₃ OH Permeability (moles CO ₂ .min ⁻¹ .cm ²) x 10 ⁻⁶	Cell Potential @100 mA/cm ² , Methanol/Air (mV)
		Operating Conditions	
		100 mA/cm ² , 60°C, 1M Methanol	
Giner, Inc. -s588-06-01		Not Tested	
Giner, Inc. -s588-07-01		Not Tested	
Giner, Inc. - s588-07-02*	588-09-01	3.4	463
Giner, Inc. - s588-08-01		Not Tested	
Giner, Inc. - s588-11-01*	588-14-01	3.3	418
Giner, Inc. - s588-11-02* ¹	588-14-02	4.3	421
Giner, Inc. - s588-11-03		Not Tested	
Giner, Inc. - s588-12-01		Not Tested	
Giner, Inc. - s588-12-02	588-14-03	0	0
Giner, Inc. - s588-12-03*	588-15-01	3.1	397
Nafion® 117 (Baseline)	554-68-00	6.5	436

¹ Low-Loaded Anode. * Selected for DMFC Testing.

Of the BCT films tested, *s588-07-02* exhibited the best DMFC performance. At a current density of 100 mA/cm² this film exhibited an ~10% increase in DMFC performance and a reduction in methanol permeation of 48% when compared to that of baseline Nafion 117. Sample *s588-12-03* exhibited the highest reduction of methanol permeation through the membrane, a **52% reduction in methanol permeation compared to Nafion 117 and fuel cell performance within 90% of the baseline film.** The films were very reproducible. Three (3) replicas of film sample *s588-12-03* were fabricated. During DMFC testing, the replicated films exhibited performance similar to the original with no increase in methanol permeation over several days of testing. Results of the replicated films were within 1% of the fuel cell performance and 2-3% of the methanol permeation value of sample *s588-12-03*. MEA *588-14-02*, fabricated with a low-loaded anode catalyst (2 mg/cm²) showed no loss in fuel cell performance. However due to non-optimized bonding conditions used to attach the electrode structures to the membrane, the film may have been slightly damaged resulting in a slightly lower exclusion rate (33% lower than that of the baseline). Higher fuel cell performance is expected from these films with the development of optimized electrode structures.

4.1.4 Scale Up and Life Testing

To function effectively in a fuel cell, the membrane must provide stable performance over an extended period of time. A brief life test was run on Sample *s588-07-02*, and is shown in **Figure 2**. In this figure, the fuel cell was operated continuously for a 100-hour period; methanol was added periodically to make up for that consumed electrochemically. Stable performance was obtained during the course of the life test. Methanol crossover was measured periodically and remained stable during the 100-hour life test.

All testing reported above was conducted using an active cell area of 25 cm². New membranes were fabricated having an 80-cm² active area, tested, and results compared to those of the smaller area MEAs. Results are shown in **Figure 3**. Almost identical performance was observed for the two different active-area MEAs, indicating (1) no loss in membrane properties during the scale up, and (2) similar flow distribution across the larger active area fuel cell. A 100-hour life test was also run using the 80 cm² MEA. Results are shown in **Figure 4**. As with the 25-cm² active area hardware, stable performance was obtained.

4.1.5 DMFC Stack Testing

A total of 5, 80 cm² MEAs identical to that shown in **Figure 3** above were fabricated and assembled into a 5-cell DMFC stack. Subsequent to a short break-in period, this stack was subjected to a 100-hour life test, with results shown in **Figure 5**. Stable performance was obtained throughout the life test. This test differed from those two described above in that the fuel cell was only operated during the day, and shut down at night. This was primarily for safety considerations as the methanol reservoir did not have sufficient capacity for overnight-unattended operation. This is the primary reason for the slight variations in stack performance.

Figure 2. 100 Hour Life Test, 25 cm²

Figure 3. DMFC Performance of Low-Graft Membranes with Different Active Areas

MEA 588-31-06

Life Test Operating
Conditions:

Film Sample s588-28-05
Continuous Operation
(@100mA/cm²)
1M CH₃OH/Air Amb.
60°C Cell Temperature
No Saturator
80 cm² Active Area

Figure 4. 100-Hour Life Test, 80 cm²

5-Cell Stack
100-Hour Life-Test

Film Series s588-28&33
Operating @100mA/cm²
1M CH₃OH/Air Ambient
60°C Cell Temperature
No Saturator
80 cm² Active Area/Cell

Methanol Permeation after 100 hours of
operation (moles CH₃OH/min.cm²)
@100 mA/cm²:

s588-28&33 = 2.2
Nafion 117 = 6.5

Figure 5. 5-Cell Stack 100-Hour Life Plot

Methanol permeability was measured periodically during the stack life test. An average 66% reduction in crossover was observed when measuring the CO₂ in the stack exhaust; due to the use of a stack, individual MEA crossover could not be measured. The 66% reduction is even lower than that obtained on the individual MEAs measured previously.

4.2 Economic Analysis

In order to be economically competitive with the internal combustion engine, the complete MEA must have a cost on the order of \$10/kW, in high volume production. A preliminary cost analysis was conducted, estimating the cost of the advanced membrane in limited production volumes. Because catalyst loadings have not been identified, the costs are for membrane only. Results to date are as follows.

Base film Cost: The cost is dependent on the base film type and gauge. Thinner films are proportionately lower in cost. With partially or fully perfluorinated polymers the cost differential is significant; a 0.05-mm film is half the cost of a 0.10-mm film because these resins are sold on a weight basis.

Radiation Costs: Beta (Electron Beam) radiation costs are relatively low when used on a production basis. BCT can process continuous films for pennies per square foot at doses above 50 Megarads.

Monomer Costs: Styrene, alpha-methylstyrene, DVB and TAC when used in production quantities for grafting and crosslinking contribute only pennies per square foot to the membrane cost.

Films and Processing Cost: As presently envisioned a fast rate, i.e., one in which the graft can be completed in less than 2 hours is amenable to an automated in-line continuous process. Our results to date show that styrene can be grafted in less than 2 hours. Our results also show that we can use the same monomer solution a number of times for grafting reactions.

Cost estimates per ft² for films and processing of films for the above are as follows:

Base Films	\$0.64 to 0.90
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Radiation in Nitrogen Crosslinking	
---------------------------------------	--

30 Megarad	\$0.12
------------	--------

50 Megarad	0.18
------------	------

Activation Dose	
-----------------	--

3 Megarad	0.04
-----------	------

6 Megarad	0.06
-----------	------

9 Megarad	0.08
-----------	------

Monomer cost per pound are as follows

Styrene	0.50
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Alpha-methylstyrene	1.00
---------------------	------

DVB	3.00
-----	------

TAC	5.00
-----	------

Waste Disposal: If as anticipated, the waste solutions from our grafting process can be polymerized to a solid polymer then waste costs are virtually eliminated. Styrene solution used in the present grafting process is currently being polymerized on a lab scale to form a solid inert polymer and disposed of as non-hazardous waste.

Sulfonation: The sulfonation cost can be relatively expensive since we must use solvent and dispose of waste sulfonation products. Solvent recovery is possible, but at a capital expense. Previous estimates indicate a cost of approximately \$1.80/m² (\$0.17/ft²). For sulfonation of a 25% grafted 0.05-mm membrane, the total waste cost would probably equal about \$2.20/m² (\$0.20/ft²). If large-scale production were anticipated then the investment in solvent recovery equipment would be justified.

Estimated Manufacturing Costs: If the membrane can be manufactured on a continuous basis and the monomer can be reused once, the materials and manufacturing operating costs will be significantly reduced. Amortization of equipment will depend on volume and overhead costs. It is not possible to accurately estimate a true manufacturing cost at this point in time. It is, however, possible to offer an educated estimate based on our past experiences in manufacturing battery and electrodialysis membranes. **The process, as envisioned for limited production (up to several hundred thousand ft² per year), would afford membranes with a price range of \$11 to \$21/m² (\$1 to \$2/ft²) or \$4 to \$9/kW.**

4.3 Discussion

Examination of the data in Figure 1 and Table 3 shows that membranes exhibiting a weight gain of ~16 to 26% during the grafting process resulted in high methanol exclusion compared to Nafion 117. Data obtained during a 100-hour 5-cell stack life test demonstrated the rate of methanol crossover through these membranes was reduced up to 90% (33% of that obtained with Nafion). Fuel cell performance obtained with these membranes was within 90% or higher of that obtained with Nafion. This data is extremely encouraging, and is providing direction as to the path to be followed in a Phase II program to further reduce methanol crossover.

The resistance of the membranes in Figure 1 is only a factor of 2, at worse, higher than that of the Nafion baseline cell, but well below the DOE goal of 0.2 ohm-cm² for specific resistance values. We suspect the slightly higher resistance is due to contact resistance with the advanced membranes. Efforts will be conducted in a follow-on Phase II program to decrease this resistance value by refining the bonding conditions used to prepare the MEA.

One of the MEAs in Figure 1, No. s588-11-02 used an anode catalyst with a 2-mg/cm² loading, as compared to the 4-mg/cm² loading used in all other testing. This fuel cell demonstrated a minimal drop-off in performance with the decreased loading, compared to cells with the standard 4-mg/cm² loading.

5.0 ESTIMATES OF TECHNICAL FEASIBILITY

The results obtained in our Phase I program have shown it is possible to simultaneously reduce methanol crossover in a DMFC while obtaining DMFC performance comparable to that obtained using a Nafion membrane as the electrolyte. **Results presented in Table 3 and Figure 1 demonstrate that it is possible to significantly reduce methanol crossover ($\geq 90\%$ exclusion). The methanol crossover is reduced by more than 66%, compared to baseline Nafion 117, with no loss in fuel cell performance.** This was accomplished by treating a fluorinated base film with only 2 Mrad of radiation, and crosslinking with DVB only to result in a weight gain of $\sim 25\%$. Previous membranes, with weight gains of 50% or higher, resulting in very open structures that had high fuel cell performance, but lacked sufficient methanol exclusion. Reducing the extent of grafting to $\sim 25\%$ results in reduced crossover with high performance. This approach warrants additional investigation in a Phase II follow-on program, to identify grafting and crosslinking conditions to further reduce the extent of methanol crossover.

In addition, one of the membranes presented in Figure 1 had a reduced anode catalyst loading of 2 mg/cm^2 , compared to the baseline 4-mg/cm^2 loading used in all other testing. No major differences in DMFC performance were observed with the reduced anode loading. Additional work in this area is recommended for Phase II follow on program. Efforts are also recommended to reduce the cathode loadings that should be easier to achieve with low crossover membranes.

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APPENDIX A

Initial membranes prepared during this program primarily used partially fluorinated as a base film. BCT did not disclose preparation conditions of these membranes to us so they are not summarized below. The preparation conditions were varied so as to evaluate the effect of select parameters on membrane performance. None of these membranes were outstanding, with crossover values greater than that of baseline Nafion, and DMFC performance, at best, only 84% that provided by Nafion.

The second batch of materials received from BCT was fabricated using partially and fully fluorinated base films. **Table A1** summarizes the membrane samples, listing the radiation doses and concentration of crosslinking agents used during membrane fabrication. The weight gain of the base film after processing is also listed in the last column of the table. As will be seen later, this is an important parameter in the development of a high-methanol exclusion membrane. The purpose of these membranes was to determine the effects of crosslinking variables on membrane properties, including the effect on methanol permeability.

Table A1. List of Films Tested

Membrane Sample ID	Base Crosslinking Radiation (Mrad)	Styrene Grafting %DVB/TAC	Post-crosslinking Radiation (Mrad)	% Weight Gain
BCT - G42-2				
BCT - G42-3				
BCT - G42-4				
BCT - 9627TM-32	50	0		~ 60
BCT - 9627TM-34	30	1.5		~ 54
BCT - 9627TM-35	70	2.0	0	~ 72
BCT - 9627TM-36	50	2.0	0	~ 67
BCT - 9627TM-37	30	2.0	0	~ 28
BCT - 9627TM-38	70	2.0	0	~ 35
BCT - 9627TM-40	30	2.0	0	~ 70
BCT - 28A	30		20	~ 150
BCT - 28B	30		10	~ 156
BCT - 28C	30		0	~ 100
BCT - 29A	50		20	~ 100
BCT - 29B	50		0	~ 100
BCT - 29C	50		10	~ 100

treatments between the grafting and sulfonation steps. Processing conditions for *G42-2*, *G42-3* and *G42-4* are unknown.

DMFC performance and permeability data obtained during testing of the BCT membranes is shown in Figure A1 and in Table A2. Test results obtained with Nafion 117, tested in the same fuel cell hardware, are included as a baseline comparison.

Figure A1. Complete DMFC Evaluation of Advanced Membranes

The best DMFC performance from this batch of base films was obtained with membrane 9627TM-32. The fuel cell performance of this membrane was equivalent to that of the baseline Nafion 117 membrane. However, this membrane exhibited ~30% higher methanol permeability than Nafion 117. Although membranes 9627TM-35 through 9627TM-40 have low methanol permeability, fuel cell performance was poor due to the high specific resistivity of these samples. Membrane samples 28A through 29C also indicated a lower methanol permeability rate than previously tested batches of BCT membranes of the same type. The methanol permeability rates of membranes 28A-28C were 3.9 to 12.8% lower than the baseline Nafion 117. Permeability of other membranes was in the same range as baseline Nafion 117.

Table A2. Summary of Direct Methanol Fuel Cell Testing

Membrane Sample ID	MEA#	CH ₃ OH Permeability (moles CO ₂ .min ⁻¹ .cm ⁻²) x 10 ⁻⁶	Cell Potential @100 mA/cm ² , CH ₃ OH/Air (mV)
		Operating Conditions	
		100 mA/cm ² , 60°C, 1M Methanol	
BCT - G42-2		NT	NT
BCT - G42-3	554-61-01	NT	429
BCT - G42-4		NT	NT
BCT - 9627TM-32	554-60-01	NT	465
BCT - 9627TM-34	554-60-02	NT	433
BCT - 9627TM-35	554-67-01	2.5 @20 mA/cm ²	0
BCT - 9627TM-36	554-67-02	No performance	0
BCT - 9627TM-37	554-67-03	No performance	0
BCT - 9627TM-38	554-67-04	No performance	0
BCT - 9627TM-40	554-67-05	No performance	0
BCT - 28A	554-67-06	4.5	407
BCT - 28B	554-67-07	4.6	437
BCT - 28C	554-67-08	No performance	0
BCT - 29A	554-67-09	10.1	410
BCT - 29B	554-67-10	5.2	423
BCT - 29C	554-67-11	4.5	423
Nafion [®] 117	554-68-0	6.5	436

Based on results of this evaluation, another batch of candidate advanced membranes was prepared by BCT. This group, summarized in **Table A3**, was prepared using systematic variations in processing parameters to determine their effect on overall membrane properties. The generalized results for this group of materials follows. To determine the trends in membrane characteristics, processed films have been grouped into the following categories:

Table A3. List of Additional Membranes

Membrane Sample ID	Base Crosslinking Radiation (Mrad)	Styrene Grafting %DVB/TAC	Post crosslinking Radiation (Mrad)	% Weight Gain
BCT - 9627TM-59	0	1.5	0	~ 40
BCT - 9627TM-64	50	1.5	5	~ 90
BCT - 9627TM-65	50	1.5	15	~ 90
BCT - 9627TM-66	70	1.0	0	~ 60
BCT - 9627TM-67	50	1.0	0	~ 60
BCT - 9627TM-68	30	1.0	0	~ 60
BCT - 9627TM-69	30	1.5	20	~ 93
BCT - 9627TM-70-2	30	1.5	10	~ 90
BCT - 9627TM-71-2	50	1.5 + 2.0% DVB/TAC second chemical graft w/ no styrene	0	~ 90
BCT - 9627TM-72	30	1.5 + 2.0% DVB/TAC second chemical graft w/ no styrene	0	~ 90
BCT - 9627TM-74	30	1.5	0	~ 60
BCT - 9627TM-75	50	1.5	0	~ 60
BCT - 9627TM-76	70			
BCT - G85-3	information given.			~ 50

Base film processed by pre-crosslinking, post-crosslinking, and chemical grafting: Fully-fluorinated base films 9627TM - 64 and 65, and partially-fluorinated base films 9627TM - 69 and 70-2, were processed by pre-crosslinking, grafting, and post-crosslinking the samples prior to sulfonation. Previously we had seen that increasing the pre-crosslinking and/or post-crosslinking radiation doses during partially fluorinated base film processing resulted in improved IEC and specific resistivity values. In this case the partially fluorinated base film, post-crosslinked with the lower radiation dose, resulted in improved specific resistivity. This may likely be due to the length of processing. A second explanation is that a skin effect may have developed on the outer surface of the film processed with the higher radiation dose. Samples 9627TM - 64 and 65 exhibited low specific resistivity and high IEC values. Specific resistivities of these membranes were comparable to that of the baseline Nafion 117 membrane. The sample processed with the lower post-crosslinking dose has slightly improved IEC and specific resistivity properties. High methanol permeation (results later) was detected during fuel cell operation of the fully fluorinated based membranes. The high permeation is a result of the high water content within the membranes.

Base film that has been pre-crosslinked and chemically grafted: Similar to the partially fluorinated samples discussed above, lower radiation doses resulted in improved specific resistivity and IEC properties. Partially fluorinated samples 9627TM - 74, 75, and 76 were base cross-linked with 30, 50, and 70 Mrad, followed by chemical grafting with 1.5% DVB/TAC. An increase in pre-crosslinking radiation resulted in a higher specific membrane resistivity and lower IEC. Pre-crosslinked partially fluorinated membranes 9627TM - 68, 67, and 66, pre-crosslinked to 30, 50, and 70 Mrad and followed by a chemical grafting with 1.0% DVB/TAC did not show any particular trend, however 9627TM - 66, pre-crosslinked with the higher E-beam output of 70 Mrad, resulted in the highest specific resistivity. Sample 9627TM - 74, having lowest specific resistivity of the group (0.289 ohm-cm^2) and one of the lowest water contents of the partially fluorinated base films (69.7%) did not exhibit improved crossover properties during fuel cell operation.

Pre-crosslinked base films grafted twice in separate chemical solutions: The fully and partially fluorinated pre-crosslinked base films, 9627TM - 71-2 and 72, were grafted in two separate solutions. Initial grafting was performed in a solution of styrene- 1.5%DVB/TAC followed by grafting in 2.0%DVB/TAC (styrene free). The specific resistivity of the fully fluorinated sample was 0.325 ohm-cm^2 while that of the partially fluorinated film was greater than 1.4 ohm-cm^2 . Membranes with a specific resistivity above 0.5 ohm-cm^2 did not perform well during fuel cell operation. It appears that post-crosslinking the base film at select doses is required for improved film properties.

Base film samples that have been processed via a single chemical graft: Sample 9627TM - 59, processed in a single grafting solution of styrene-1.5%DVB/TAC, also had a high specific resistivity (1.35 ohm-cm^2). No performance on this membrane was obtained during fuel cell operation.

Films fabricated via BCT's new water emulsion process: Fully fluorinated base samples G87-2 and G94-1, processed via a water emulsion process had the lowest water contents of all samples. Specific resistivities of the fully fluorinated base samples were double that of the baseline Nafion 117 membrane. Although resistivities were high, they were in the acceptable range for fuel cell operation. Sample G87-2 exhibited 20% lower methanol permeability than the baseline sample at a current density of 100 mA/cm^2 , however performance also dropped by 26% compared to Nafion 117. Another fully fluorinated sample, G85-3, processed using the same method, had a high resistivity and did not perform well during fuel cell operation.

Performance data for membranes in this group which were evaluated using complete DMFC testing conditions are summarized in Table A4 and in Figures A2 to A6.

Table A4. Summary of Direct Methanol Fuel Cell Testing

Membrane Sample ID	MEA#	CH ₃ OH Permeability (moles CO ₂ .min ⁻¹ .cm ⁻²) x 10 ⁻⁶	Cell Potential @100 mA/cm ² , CH ₃ OH/Air (mV)
		Operating Conditions 100 mA/cm ² , 60°C, 1M Methanol	
BCT - 9627TM-59	554-83-01	No FC Performance	0
BCT - 9627TM-64	554-83-02	8.4	453
BCT - 9627TM-65	554-83-03	7.5	435
BCT - 9627TM-66	554-86-05	No FC Performance	0
BCT - 9627TM-67	554-86-07	9.7	393
BCT - 9627TM-68	554-83-07	No FC Performance	0
BCT - 9627TM-69	554-87-01	20+ Film fractured	0
BCT - 9627TM-70-2	554-86-06	20+ Film fractured	0
BCT - 9627TM-71-2	554-87-02	20+ Film fractured	350
BCT - 9627TM-72	554-86-04	No FC Performance	0
BCT - 9627TM-74	554-83-04	6.9	422
BCT - 9627TM-75	554-83-05	6.1	404
BCT - 9627TM-76	554-83-06	No FC Performance	0
BCT - G87-2	554-86-01	5.6	323
BCT - G94-1	554-86-02	No FC Performance	0
BCT - G85-3	554-86-03	No FC Performance	0
Nafion® 117 (Baseline)	554-68-00	6.5	436

Figure A2. DMFC Performance of base film processed by pre-crosslinking, post-crosslinking, and chemical grafting.

Figure A3. DMFC Performance of pre-crosslinked and chemically grafted base films.

Figure A4. DMFC Performance of pre-crosslinked base films grafted twice in separate chemical solutions.

Figure A5. Performance of base film samples that have been processed via a single chemical graft.

Figure A6. Performance of films fabricated via BCT's new water emulsion process.

Examination of the characterization data and crossover data from the membranes summarized in Table A3 above resulted in an important finding: a **decreased** graft within the membrane resulted in **decreased** methanol crossover. To verify this hypothesis, the membrane samples listed in **Table A5** were prepared and evaluated. In these samples, the amount of grafting within the membrane, reflected in the weight gain listed in the last column, was reduced considerably from that used previously. In addition, these membranes did not contain TAC. Fuel cell performance data and crossover data are provided in **Figures A7 and A8**, and in **Table A6**.

Table A5. Description of Additional Membranes

Membrane Sample ID	Base Crosslinking Radiation (Mrad)	Styrene Grafting %DVB	Post-crosslinking Radiation (Mrad)	% Weight Gain
BCT - 9627TM-86				
BCT - 9627TM-91				~ 22
BCT - 9627TM-92	Processed similar to 28 and 29 but using 5 mil			
BCT - 9627TM-93				
BCT - 9627TM-94		High crossling and high graft		
BCT - 9627TM-95		0.5		~ 38
BCT - 9627TM-97				~ 30
BCT - 9627TM-104		0.5		~ 30
BCT - 9627TM-105		1.0 + TAC		~ 30
Giner, Inc. - 588-04-01	2	1	0	
Giner, Inc. - 588-04-02	3	1	0	
Giner, Inc. - 588-04-03	4	1	0	
Giner, Inc. - s588-06-01	2	1	0	1.4
Giner, Inc. - s588-07-01	2	1	0	0.7
Giner, Inc. - s588-07-02*	2	1	0	25.8
Giner, Inc. - s588-08-01	2	1	0	89
Giner, Inc. - s588-11-01*	2	1	0	19.07
Giner, Inc. - s588-11-02*	2	1	0	23.8
Giner, Inc. - s588-11-03	2	1	0	28.3
Giner, Inc. - s588-12-01	2	1	0	5.5
Giner, Inc. - s588-12-02*	2	1	0	8.2
Giner, Inc. - s588-12-03*	2	1	0	16.6

No TAC in any of films above unless listed.

Figure A7. DMFC Performance of base film processed by pre-crosslinking, post-crosslinking, and chemical grafting.

Figure A8. DMFC Performance of Low-Graft Membranes

Table A6. Summary of Direct Methanol Fuel Cell Testing

Membrane Sample ID	MEA#	CH ₃ OH Permeability (moles CO ₂ .min ⁻¹ .cm ⁻²) x 10 ⁻⁶	Cell Potential @100 mA/cm ² , CH ₃ OH/Air (mV)
		Operating Conditions 100 mA/cm ² , 60°C, 1M Methanol	
BCT - G96	554-95-02		160
BCT - G101-2	554-95-02	6.1	368
BCT - 9627TM-86	588-02-01		
BCT - 9627TM-91	588-01-02	3.3	150
BCT - 9627TM-92	588-01-04	Too brittle for testing/fractured	
BCT - 9627TM-93	588-01-03	6.5	414
BCT - 9627TM-94	588-01-05	Too brittle for testing/fractured	
BCT - 9627TM-95	588-01-01	4.1	432
BCT - 9627TM-97	588-01-06	Too brittle for testing/fractured	
Giner, Inc. - s588-07-02*	588-09-01	3.4	463
Giner, Inc. - s588-11-01*	588-14-01	3.3	417
Giner, Inc. - s588-11-02* ¹	588-14-02	4.3	421
Giner, Inc. - s588-12-03*	588-15-01	3.1	397
Nafion® 117 (Baseline)	554-68-00	6.5	436

¹ low loaded anode

Examination of the data in Figures A7 and A8, and Table A6 shows that membranes exhibiting a weight gain of ~17 to 26% during the grafting process resulted in high methanol exclusion compared to Nafion 117. The rate of methanol crossover was reduced by up to 52% of that obtained with Nafion. Fuel cell performance obtained with these membranes, especially those presented in Figure A8, was within 90% of that obtained with Nafion. This data is extremely encouraging, and is providing direction as to the path to be followed in a Phase II program to further reduce methanol crossover.

The resistance of the membranes in Figure A8 is only a factor of 2, at worse, higher than that of the Nafion baseline cell, but well below the DOE goal of 2 ohm-cm² for specific resistance values. We suspect the slightly higher resistance is due to contact resistance with the advanced membranes. Efforts will be conducted in a follow-on Phase II program to decrease this resistance value by refining the bonding conditions used to prepare the MEA.

One of the MEAs in Figure A8, No. s588-11-02 used an anode catalyst with a 2-mg/cm² loading, as compared to the 4-mg/cm² loading used in all other testing. This fuel cell demonstrated a minimal drop-off in performance with the decreased loading, compared to cells with the standard 4-mg/cm² loadings. Additional work will be conducted during the remainder of the Phase I program, and continued in Phase II, to further reduce catalyst loadings.