Final Report

160°C Proton Exchange Membrane (PEM) Fuel Cell System Development

Prepared by

Gas Technology Institute
1700 S. Mt. Prospect Rd.
Des Plaines, IL 60018-1804

L.G. Marianowski, Program Manager

TABLE OF CONTENTS

Executive Summary

This work was conducted under DOE Cooperative Agreement # DE-FC26-99FT40656, 160°C Proton Exchange Membrane (PEM) Fuel Cell System Development, in the period from September 1, 1999 to September 30, 2001. The purpose of this work was to develop a complete high temperature fuel cell. The scope involved

    (a) The development of a new high temperature polymer membrane material to cast films and fabricate membrane electrode assemblies (MEA) for testing.

    (b) A determination if the GTI-molded composite graphite bipolar separator plates are able to operate in fuel cells at temperatures up to 160°C.

The membrane tasks included defining and optimizing the process steps to produce and purify the new polymer membrane material, to cast the polymer into thin films, to fabricate membrane electrode assemblies (MEA), followed by performance testing in single cells. The Gas Technology Institute (GTI), formerly Institute of Gas Technology (IGT), conducted the work with its subcontractor, Case Western Reserve University (CWRU).

The GTI-molded composite graphite bipolar separator plates have operated successfully in 7 to 70 cell-Nafion™- membrane fuel cell stacks at the usual 60 to 80°C. The development of the molded composite graphite separator plate was advanced in a previous DOE program (DE-FC02-97EE50477). But for 160°C operation of the molded plates, various physical and electrical properties had to be confirmed, namely; surface resistivity, bulk resistivity, compressive and flexural strength, stability of dimensions and density, hydrogen permeability, and water uptake. Measurements were made from 90°C up to 160°C. Also suitable high temperature gasket materials that adhere to graphite and comply with the MEA and graphite were tested over this temperature range with gas side pressures up to 2 psi. All of the test results concluded that the GTI molded composite graphite bipolar plate properties had excellent performance characteristics for operation up to 160°C.

CWRU focused on investigating and optimizing the processing and purification conditions for the starting polymer material. They proposed a polymer that they patented, designated as ABPBI, which may have manufacturing cost advantages over other high temperature polymer candidates. They performed fundamental testing on the material to optimize polymer production. Once baseline conditions were developed, larger quantities were made by a vendor according to the specified process conditions. Samples of batches from both CWRU and the vendor were sent to GTI for casting into films, testing of membrane properties, fabrication into MEAs, and testing in fuel cells. GTI investigated film casting methods to make membranes with the best physical and chemical properties. Membrane thickness could be cast uniformly as thin as 12.5 microns and as thick as 100 microns. Proton conductivity was tested up to 160°C and found to be equal to or greater to the conductivity of commercially available Nafion™ at 60°C.

The final stage of this project focused on the fabrication of MEA's and tests in 60 cm2 single cells to optimize MEA fabrication as well as performance and endurance with CO-containing reformate fuel gases. Multiple series of MEA's were fabricated and tested to analyze specific improvements in MEA design as well as membrane additives. In this stage, progress was made as fuel cell performance improved with each cycle of MEA revision and testing, with step gains of about 80 mV. However, at the end of this program, additional performance improvements in the membrane and MEA still need to be made to increase the cell voltage by another 150 mV to reach a typical performance benchmark of 650 mV @ 400 mA/cm2.

The fuel cell tests conducted at GTI also showed that the MEA was unaffected by the presence of CO in the anode feed gas with a concentration of 1000 ppm. Over 800 hours of endurance tests were performed on MEAs operating with high ppm CO. When 1000 ppm CO was introduced, only a 15 mV performance loss was observed. When MEA's operate at 80°C, this loss would have been hundreds of millivolts. This represents the best high temperature performance to date in the literature. These first MEA's showed a decay rate of about 20 mV per 1000 hours

operation. This endurance along with the voltage performance still has to be improved to reach a viable commercial target of about 2 mV decay per 1000 hours operation. Many fabrication and doping techniques remain to be evaluated on the path of MEA optimization. Also remaining to be done in conjunction with performance and endurance gains for this high temperature MEA is to determine the costs of membrane production, of the casting process, and of the MEA fabrication process to be able to assess the commercial and economic success of this high temperature membrane. Preliminary estimates indicate reasonable costs for this MEA, but this needs to be confirmed as the processing steps mature.

Introduction and Background

The objectives of this program were

(a) To develop and demonstrate a new polymer electrolyte membrane fuel cell (PEMFC) system that operates up to 160°C temperatures and at ambient pressures for stationary power applications, and

(b) To determine if the GTI-molded composite graphite bipolar separator plate could provide long term operational stability at 160°C or higher.

There are many reasons that fuel cell research has been receiving much attention. Fuel cells represent environmentally friendly and efficient sources of electrical power generation that could use a variety of fuel sources. The Gas Technology Institute (GTI), formerly Institute of Gas Technology (IGT), is focused on distributed energy stationary power generation systems. Currently the preferred method for hydrogen production for stationary power systems is conversion of natural gas, which has a vast distribution system in place. However, in the conversion of natural gas into a hydrogen-rich fuel, traces of carbon monoxide are produced. Carbon monoxide present in the fuel gas will in time cumulatively poison, or passivate the active platinum catalysts used in the anodes of PEMFC's operating at temperatures of 60 to 80°C. Various fuel processors have incorporated systems to reduce the carbon monoxide to levels below 10 ppm, but these require additional catalytic section(s) with sensors and controls for effective carbon monoxide control. These CO cleanup systems must also function especially well during transient load operation where CO can spike 300% or more.

One way to circumvent the carbon monoxide problem is to operate the fuel cell at a higher temperature where carbon monoxide cannot easily adsorb onto the catalyst and poison it. Commercially available polymer membranes such as Nafion™ are not capable of operation at temperatures sufficiently high to prevent this. Hence this project investigated a new polymer membrane alternative to Nafion™ that is capable of operation at temperatures up to 160°C.

There are a number of other operational and cost benefits to operation at higher fuel cell temperatures. These include simplifications to the fuel processor and its sections and controls for carbon monoxide removal, the availability of a higher quality recoverable heat from the power system, and the use of smaller area heat exchangers. Furthermore optimum performance of the fuel cell would not depend on membrane water management and humidification of the fuel and air streams would not be required. Humidification and water management are not necessary with a high temperature membrane system because the new polymer does not require humidification to be proton conductive, as Nafion™ does. Taken together, the benefits of a practical high temperature membrane would make substantial reductions in the cost of PEM fuel cell power systems thereby hastening commercialization.

This program investigated two major fuel cell components necessary for a successful high temperature fuel cell system: a high temperature membrane and the bipolar separator plate. The development of a new high temperature membrane and its fabrication into a practical membrane electrode assembly (MEA) is one of the critical components needed for successful high temperature fuel cells. The layered structure of a MEA is complex with several distinct processes occurring simultaneously within it. The three major physical components that make up a MEA are the polymer membrane, with very thin catalyst layers contacting both its sides, followed by the gas diffusion-electrode backing layers. The function of all of these is interrelated in a MEA. The catalyst layer's accessibility and catalyst utilization is important for fuel cell performance, endurance, and cost. Present anode catalysts use state-of-the-art carbon monoxide-tolerant platinum alloys. In addition to the requirements for the polymer membrane and the catalyst layers, the surrounding gas diffusion layers must be able to provide strength, collect current, and retain their mass transfer functions at elevated temperatures.

The other major fuel cell component needed for a successful high temperature fuel cell is a stable, well-performing bipolar separator plate. The separator plate provides the gas and air flow fields to the MEA, a support platform for the MEA's,

2

and conduction of the electrical current of the stack. The applicability of the GTI-molded composite graphite bipolar separator plate was investigated for fuel cell operation temperatures up to 160°C. A series of tests were conducted to confirm that the necessary properties and functions of the molded plates were satisfied at temperatures up to 160°C. In addition, several gasket materials and methods were found to be able to seal these molded plates at high temperatures.

The development of the GTI-molded composite graphite bipolar separator plates was supported in an earlier DOE program (DE-FC02-96EE50477) and in a program sponsored by MOSAIC Energy, LLC. The properties of the molded plates were shown to be excellent as the molded plates have performed very well in Nafion™ fuel cell stacks operating up to 80°C. The molded composite graphite plates were shown to be highly electrically conductive, strong, and moldable to net shapes.

Discussion of Results

This report presents the results of this program in three main parts:

A. Molded Graphite Separator Plate Properties

B. Polymer Production and MEA Fabrication

C. MEA Performance Test Results

A. Molded Graphite Separator Plate Properties

The results of tests and measurements of the GTI molded composite graphite bipolar separator plate for operation at fuel cell temperatures up to 160°C are presented in Section A. The high temperature viability of the GTI molded bipolar separator plate plus the necessary gasket sealing was assessed with measurements of physical, electrical, and chemical properties over a potential fuel cell operation range from 90°C to 160°C. The series of physical and electrical measurements sought to identify any property changes at the elevated temperatures. The physical properties of interest that were measured included plate thickness, density, degree of water uptake, H_2-gas permeability, thermal conductivity, and compressive and flexural strength. The electrical properties measured were the volume or bulk resistivity and the surface resistance. Leaching studies were also conducted to determine if any component of the molded separator plate degraded.

Thickness, Density and Degree of Water Uptake

Reduction in plate thickness can destroy the integrity of a fuel cell stack. If the plates change significantly in thickness with temperature, sealing and clamping forces are affected. With a seal breached, gases will be lost to the outside and without sufficient clamping forces, electrical conductivity through the stack would be jeopardized. We found that there was no significant change in the measurements of the thickness or density of the molded plate samples before and after heating each sample up to the selected individual temperature levels of 90, 120, 140 and 160°C.

The GTI molded separator plate's physical and electrical properties depend strongly upon the density of the molded plate. If the density of the plate remains constant at operating temperatures up to 160°C, then the maximum electrical conductivity of the GTI molded plate will be retained at these elevated temperatures. The plate samples that were prepared for measurements up to 160°C were pressed to a near constant density between 1.8 to 1.9 g/cc. Separator plates with this density have shown excellent performance in 70-cell fuel cell stacks operating at 70°C in other GTI work.

The degree of water uptake of the molded plate should be small because of the high density and low porosity. Furthermore, in operation of stacks above 100°C at atmospheric pressure conditions the water present will be in vapor form. However, in the startup and shutdown of fuel cell stacks, liquid water can be present as condensate. Measurements were made to quantify the amount of water that could be held in the plates. For these tests, individual plate samples were heated at the selected temperatures of 90, 120, 140, and160°C for a significant time, and then after cooling, soaked in a 70°C water bath. The water uptake capacity of the sample plates was measured by weight differences after quickly wiping off any surface water. No significant differences in water uptake were measured between any of the molded plate samples that were first treated at the various selected temperatures.

Hydrogen Permeability

Hydrogen permeability of the bipolar separator plate is very important to minimize. If hydrogen permeability is significant, hydrogen can leak externally, which affects hydrogen distribution and utilization, or if hydrogen permeates and mixes with cathode air, at the minimum, voltage losses will occur lowering the system efficiency. The results of the hydrogen permeability measurement tests are presented in Table 1 for four plate samples treated at different temperatures before the test. A simple apparatus was made to hold and seal a one-inch diameter plate sample between two chambers, one side maintained with hydrogen at selected test pressures, and an inverted graduated cylinder in water collects any hydrogen

that permeates. The rates are very slow so each test takes a long time to collect enough hydrogen to obtain meaningful results.

The H_2 permeability apparatus test conditions of temperature and differential pressure are given on the left side of Table 1. Plate samples identified as A, B, C and D were first heat "soaked" at temperatures of 90°C, 120°C, 140°C and 160°C, respectively, then held in the apparatus at the conditions represented on the left side of the table, i.e., different hydrogen pressures and test temperatures. The 30 psi differential value (psid) was selected because it represents the highest operating pressures considered for polymer fuel cell stacks, such as vehicular applications. The 5 psid value represents typical near-atmospheric stack operating pressures for stationary applications.

For plate sample A (i.e., treated only at 90°C), the H_2 permeability for the tests conducted at a 30 psid across the plate, decreases slightly from 1.6×10^{-3} to 1.4×10^{-3} cm^3/cm^2-sec with test apparatus temperatures maintained at 120, 140, and 160°C. The H_2 permeability rate decreased about two orders of magnitude from 1.4×10^{-3} cm^3/cm^2-sec to 4.4×10^{-5} as the H_2 test pressure was reduced from 30 to 5 psid at the 160°C test temperature.

For plate sample B (i.e., treated only at 120°C), the H_2 permeability at 30 psid level decreases from 2.9×10^{-5} to 1.3×10^{-5} cm^3/cm^2-sec for the increasing test apparatus temperatures of 120 to 160°C. The H_2 permeability decreased by another order of magnitude from 1.3×10^{-5} cm^3/cm^2-sec to below detectable levels when the H_2 test pressure was reduced from 30 to 5 psid at the 160°C test temperature.

For plate samples C and D (treated only at 140 and 160°C, resp.), H_2 permeability could not be detected at any of the test conditions of differential pressure or temperature. As indicated by the data, samples C and D that were treated at 140°C and 160°C respectively did not have any detectable hydrogen permeability at any of the tested conditions. It is evident that as the temperature increases, the hydrogen permeability decreased for all tested samples.

6

Table 1. HYDROGEN PERMEABILITY OF THE MOLDED BIPOLAR PLATES

Apparatus Test Conditions		H_2 Permeability, $(cm^3/cm^2\text{-sec})$			
H_2 Differential Pressure (psid)	Temp, (°C)	Sample A[†]	Sample B[†]	Sample C[†]	Sample D[†]
30	120	1.6×10^{-3}	2.9×10^{-5}	ND[††]	ND
30	140	1.5×10^{-3}	2.9×10^{-5}	ND	ND
30	160	1.4×10^{-3}	1.3×10^{-5}	ND	ND
15	160	1.9×10^{-4}	4.2×10^{-6}	ND	ND
5	160	4.4×10^{-5}	ND	ND	ND

[†] Samples A, B, C and D were each heated and held at 90, 120, 140 and 160 °C resp.

[††] ND = not detectable (i.e., below $1 \times 10^{-6} cm^3/cm^2\text{-sec}$)

Thermal Conductivity

Thermal conductivity measurements of the molded bipolar plate samples were sent to an outside laboratory that had the necessary thermal conductivity apparatus. The thermal conductivity values at various temperatures were determined for both dry and water-saturated plates (treated up to 160°C). A sample of the state-of-the-art POCO™ graphite that is used in many fuel cell stacks was also measured for comparison purposes. The results of the testing indicate that the in-plane thermal conductivity value of the GTI composite graphite molded separator plates is about 93% that of POCO™ graphite value at 85 W/m-K (0.014 Btu/sec-ft-°F), while the through-plane thermal conductivity value is about an order of magnitude lower than POCO™ graphite. POCO™ graphite thermal conductivity is uniform in both directions since it is made from synthetic graphite material.

The thermal conductivity values for the GTI composite graphite molded plates in comparison to the commercial POCO™ graphite fuel cell plate material was found

to follow the same trend as the electrical conductivity values. The magnitude of the values measured indicate that the GTI molded plates will be able to operate at the higher fuel cell stack temperatures and conduct heat sufficiently to provide a uniform temperature distribution within the fuel cell stack.

Strength and Compression

Compressive and flexural strength tests conducted at GTI on the molded plate samples indicate that the molded plates are strong and show a flexibility ideal for fuel cell stacks. Sufficient compressive strength of the bipolar separator plate is required so as to not deform or crack under the compressive or clamping pressures of the fuel cell stack. A compressive strength of 1300-psi was determined for the plate samples, which is more than enough for the approximate 200 psi pressures exerted by the fuel cell stack clamping forces.

A degree of flexural strength is desired for the molded bipolar separator plates to withstand potential bending forces exerted within or on the fuel cell stack. The flexural strength property is critical when many plates are stacked in a fuel cell. If the plates are rigid or brittle, then clamping irregularities, vibration, or shock loads can cause the plates in the stack to develop cracks or lose seals. The flexural strength values measured for the GTI molded plate samples are from 4000 to 6000 psi for plate samples that were preheated at 160°C. Also to confirm the inherent flexibility of the molded plates, mid-span deflections were measured. About 0.125-inch deflection at the middle of an 11-inch span of a molded separator plate was typically measured. By comparison, POCO™ graphite is rigid and will crack.

Volume Resistivity and Conductivity

The volume resistivity of separator plates for use in fuel cell applications is of critical importance in conducting current with minimum losses. The entire stacked plate ensemble needs to be efficient in current transmission, which means minimizing the resistance losses in both separator plates and MEA's. The various components that make up a fuel cell all add finite resistances and it is only possible to reduce the resistances to the minimum. In particular, each separator plate acts

8

as a current collector for each individual cell and also as planer connectors to the power takeoff terminals at the ends of the stack.

The volume resistivity of the treated molded plates was measured according to ASTM C-611 standard procedure. This procedure consists of placing the molded plate sample between a pair of electrodes separated by a known distance, imposing a precise current and measuring the potential difference between the electrodes, i.e., the voltage drop. The resistivity (ρ) of the plate is determined from these measurements.

The volume resistivity (ρ) is calculated from Equation 1.

$$\rho = R \times A / L \qquad\qquad (1)$$

where:

ρ = Resistivity, Ω-cm

R = Resistance, Ω

A = Cross-sectional area, cm^2

L = Distance between the electrodes, cm

The volume conductivity (σ) is calculated by Equation 2 and the units are expressed as Siemens, S = 1/Ω.

$$\sigma = 1/\rho \qquad\qquad (2)$$

where:

σ = Volume Conductivity, S/cm

ρ = Resistivity, Ω-cm

Table 2 shows that the volume resistivity values, ρ, increased from 1.2 to 2.9 mΩ-cm in the tests with increasing temperatures of the molded plate. The volume conductivity, σ, consequently decreased from 833 to 346 S/cm. For comparison, POCO™ graphite materials have room temperature volume resistivity values in the range of 1.0 to 2.5 mΩ-cm, and flat copper plate values are much lower about 0.003 to 0.004 mΩ-cm. The GTI molded bipolar plates have volume resistivity values that are very close to commercially available POCO™ graphite. Hence,

9

with these electrical conductivity values, the GTI plates would perform similarly to commercially available synthetic graphite from room temperature to 160°C operation. DOE has specified minimum conductivity values of 100 S/cm for their vehicular fuel cell applications and the excellent performance of the GTI molded plates at 60 to 80°C, has been confirmed in the DOE program DE-FC02-96EE50477.

Table 2. VOLUME RESISTIVITY AND CONDUCTIVITY[†]
OF THE MOLDED BIPOLAR PLATES

	90°C	120°C	140°C	160°C
Volume Resistivity (mΩ– cm)	1.2	2.0	2.4	2.9
Volume Conductivity (S/cm)	833	500	417	345

[†] for vehicle applications, DOE specified volume conductivity to be greater than 100 S/cm

Surface Resistance

Surface or contact resistance of the separator plates is another important property of stacked plates in fuel cell stacks. The surface resistance of the treated plate samples was measured using a GTI-devised method because no recognized standard technique was found to be suitable for measuring surface resistance of these molded separator plates. The method yields relative values that can be compared to certain materials used in fuel cells, thus correlating to actual fuel cell performance. The resistance is measured between two-points of a gold plated probe held in contact with the plate surface with a weight to apply a constant probe force.

Table 3 presents the surface resistance values that were measured at room temperature for the plate samples that were treated at various temperatures. As can be seen, the values increase from 184 mΩ to 200 mΩ for the samples heated at 90°C to 140°C temperatures, but a lower value of 170 mΩ was measured for the plate sample treated at 160°C. This value remains unexplained, however, the

entire range of values is within 15% and thus may not be significant. For comparison, the room temperature surface resistance values measured for POCO™ graphite is 140 to 150 mΩ, which is close to the values of the molded plates. This difference between GTI molded graphite plates and POCO™ graphite plates are not expected to significantly affect the electrical conduction properties of the molded plates. Fuel cell performance will be related to surface resistances of the stacked components, however, more importantly, surface flatness of all the molded separator plates, the clamping forces, plus the contact characteristics of the MEA's. The inherent flexibility of the GTI molded plates will help significantly in effecting a better contact with MEA's and the other separator plates.

Table 3. SURFACE RESISTANCE OF THE MOLDED BIPOLAR PLATES

	90°C	120°C	140 °C	160 °C
Surface Resistance (mΩ)	184	190	200	170

Seal Evaluation

After the set of measured molded plate properties were confirmed to be suitable for elevated temperature fuel cell operation, various gasket materials were investigated and tested between molded flow field separator plates. A fuel cell stack requires gaskets or other seals, but the higher temperature operation imposes more requirements on gasket materials because of the increased expansion and contraction from cold startup to operation. Several suitable materials were found to maintain a seal against the molded graphite plates. Test separator plates with a 60 cm^2 active area were molded and used for the sealing trials and subsequent fuel cell tests. The fuel cell tests were the first conducted with the new high temperature membrane that GTI fabricated into MEA's. Following single cell testing, several multiple-cell stacks were assembled with place holding dummy MEA's and heated to 160°C to determine if the sealing materials and compounds were gas-tight. A suitable and easily applied gasket

material was found capable of sealing cells at 160°C with an internal gas pressure of 2 atmospheres. This gasket material was used throughout the subsequent fuel cell tests conducted with the high temperature MEAs fabricated as described in the following section.

B. Polymer Production and MEA Fabrication

As was mentioned earlier, MEA (membrane electrode assembly) optimization is a complex task that requires iteration between the process steps of polymer production, membrane casting, MEA fabrication, and cell assembly and testing. This MEA fabrication and test phase began with an investigation of the production of the new polymer material along with optimization of its processing and casting methods.

Polymer Production Optimization

Several high temperature polymer membranes are described in the literature, and recently, a very promising polymer was advanced by Hoechst-Celanese, a non-fluorinated polymer called polybenzimidazole, (PBI). Discussions with Hoecsht-Celanese indicated that the cost of PBI polymer manufacturing might be higher than desired for commercial fuel cells. Discussions with Case Western Reserve University, who developed the original PBI polymer and licensed its patents to Hoecsht-Celanese, indicated that an alternate polymer formulation might have manufacturing cost advantages over PBI if it would perform as well. This polymer was also developed at Case and is designated as AB-PBI for poly (2,5-benzimidazole).

While GTI was investigating molded separator plate properties in this program for suitable use at 160°C, Case Western Reserve University (CWRU) under subcontract, was investigating the process steps to produce ABPBI polymer material for GTI to cast into membranes. Over the course of this project, CWRU had delivered samples from many different batches for GTI processing into membranes and MEA's. Each of the batches was produced using different

12

procedures that yielded polymers of different intrinsic viscosities and altered compositions. The viscosity values ranged from a low value of 1.85 dL/g, which is similar in viscosity to water, up to 5.64 dL/g, which is similar to a 50% glycerol solution. The early batches had viscosities near the lower end of this range because of the chosen synthesis procedures. After a few months of trials and re-formulations, the polymer could be synthesized in much higher viscosities that allowed better control of the cast film properties. This work was done at CWRU and both the raw monomer steps and the final polymer purification steps were studied to obtain improved results. They also varied temperature, heating modes, and mixing times to develop the optimal polymer material for casting. The viscosity of the polymer is one of the key properties that influence casting procedures to make thin and uniform thickness membranes. The membrane material that is cast into thin uniform films is very important component, but it is only one component of the three-component MEA.

MEA Requirements

Three main components comprise a membrane electrode assembly: the membrane film, the catalyst layers, and the gas diffusion electrode backing layers. While developing a novel proton conducting MEA, the membrane is the most discussed research. Yet the active catalyst layers, usually dispersed with an ionomer of the membrane, and the backing layers are just as vital to the MEA performance. Obviously, the membrane must be proton conductive for a fuel cell to operate. It also must be chemically and physically stable for long-term operation. For example, the membrane must not allow acid or other components to leach out, which can cause the proton conductivity to decrease as well as deactivate the catalyst. The catalyst layer is equally important because this layer must also be chemically and physically stable. The ionomer-to-catalyst ratio is crucial for maximum catalyst activity. Finally, the backing layer must allow gases to pass to and products away from the catalyst layer; it must also support the membrane and catalyst layer and act efficiently as a current collector. The variables that influence the performance of this layer are discussed in the following

section, as the optimization and interrelation of all three of these components was studied.

Polymer Membrane Casting

The first period of membrane casting dealt with polymer batches with intrinsic viscosity values less than 2 dL/g. The polymer material, when dissolved, was slightly more viscous than water so it had to be cast in a retaining apparatus to achieve a uniform membrane thickness. When cast, these films were approximately 25 microns thick. However, these were relatively weak, so that when fabricated into MEA's for fuel cell tests, two layers of this material were found to be necessary so that it would not tear.

The polymer batches received at the end of the program from CWRU all had intrinsic viscosities greater than 3.8 dL/g. It was learned that the membrane materials produced from these batches had to be treated differently than the earlier batches. These, when dissolved, were much more viscous to handle and varied slightly in color. The thicker batches appeared more yellow-orange in color whereas the less viscous batches were closer to a rust brown color. The thicker batches could be cast on a flat glass without a retaining wall because of the higher viscosity. Single membranes could be cast up to 100 microns but thinner membranes are desired to minimize resistive losses. However, until the membrane strength is optimized, most tests were conducted with the slightly thicker membranes. It is understood that thicker membranes cause the MEA internal resistance to be higher. Methods were altered to cast thinner membranes using the higher viscosity polymer materials. A glass rod was successfully used to manually distribute the material uniformly over a large area, much like a calendaring manufacturing process. With this method, membranes could be cast as thin as 12.5 microns. Due to the higher viscosity values, these thin films also had enough physical strength to operate under fuel cell conditions.

It was confirmed by experimentation that additional properties were also better with the higher viscosity material, such as the chemical stability and the proton conductivity of the membranes. Also by supplementing a diluted polymer with

14

various additives, GTI has been able to increase the chemical stability significantly as well as the physical stability. By varying the composition of the pre-cast polymer solution in this way the proton conductivity at 120 °C increased so that it was greater than that of commercially available Nafion™ at 60°C. Figure 1 shows various samples of cast membranes after they had been cast and dried before MEA assembly.

Figure 1. Photo of Cast Membrane Films.

Catalyst Layer

The catalyst layer is deposited from a mixture that consists of nano-sized platinum catalyst supported on carbon particles, the ionomer material of the membrane, and a solvent that allows the catalyst to behave like an ink. In this program, the catalyst that was used was supplied by Johnson-Matthey Co. Both platinum and platinum-ruthenium CO-tolerant catalysts were used. At 160 °C operation, there

was no difference between either of these catalysts, confirming that the CO-tolerant catalyst is not necessary at 160°C operation.

For these experimental trials, the catalyst loading was kept at a fairly high loading between 0.5 and 0.75 mg/cm^2 for the anode and the cathode to disperse sufficient catalyst. Later in the development, this loading would be reduced. The ionomer functions as a binder for the catalyst and a proton conduit between the catalyst and polymer membrane. The ratio is very important because too much ionomer can cover up the catalyst sites and significantly decrease the fuel cell performance. The amount of ionomer in the catalyst layer was varied between 2 and 20%. The solvent used was the same solvent used in the membrane production, so that it would not cause any problematic interactions between the membrane and catalyst layer. Just as in the process of casting membranes, catalyst layer preparation methods were modified because of the different viscosity polymer materials. For instance, as more viscous polymer materials were tested, the catalyst layers would sometimes mudcrack while drying. To circumvent this common problem, ink-painting methods of catalyst application had to be varied. For example, higher concentrations of solvent were sometimes used to allow the polymer to relax for a longer period of time while the solvent slowly evaporated. Various additives were also evaluated to help improve performance and endurance of the MEAs in fuel cell operation.

Backing Layer

The last major component of the MEA to optimize was the backing layer. The properties of this layer are sometimes overlooked while developing an MEA from any novel proton conducting membrane material. The backing layer plays an important role and is linked to the other layers in support of the assembly of a higher performance MEA. Gas diffusion to and from the membrane and efficient current collection are extremely important, especially at practical high current density operation. The backing layer has to perform in two different regimes. The anode has hydrogen diffusion while the cathode has 20% oxygen in nitrogen diffusing counter to the flow of product water vapor. GTI tested a backing layer

developed in-house versus other products available commercially. MEAs made from the GTI backing layer have performed better with longer endurance than any of the other materials tested.

Layers Synergistically Linked

As stated previously, the functions of the three major components of the MEA assembly, the thin membrane, the catalyst layer, and the backing layer are all dependent upon one another and synergistically linked. During the early iterative search for the optimum high temperature MEA, whenever one component of the MEA or its properties was changed, the remaining two components had to be modified as well to maintain or regain optimal performance. For example, just because one backing layer design peforms well with the low viscosity membrane material, does not ensure that it would work well with a similar, but higher viscosity material. Each set of modifications required time to be systematically tested for physical, performance, or endurance improvements under fuel cell operating conditions.

C. MEA Performance Test Results

CO Tolerance and Improvements

In the iterative modification and testing period, many improvements were made from the first MEA tested under fuel cell conditions to the final MEA made in this project. For any MEA, baseline tests were always run with pure hydrogen to the anode and air to the cathode as standard procedure. Also all fuel cell tests in this program were run at an operating temperature of 160°C and fuel/oxidant stoics of 1.2/2.0. The MEA active area was 49 cm^2 (7 x 7 cm) with high temperature sub gasket and gasket materials. MEAs were typically operated using pure hydrogen for at least one day (24 hours) to obtain the baseline for comparison between MEA's before switching to a reformate fuel gas (80% H_2, 20% CO_2, and up to 1000 ppm CO). The first MEA that was fabricated yielded an open circuit voltage of just over 400 mV whereas the latest versions were capable of over 900 mV, which is close to the performance of Nafion™. Not only has open circuit voltage improved
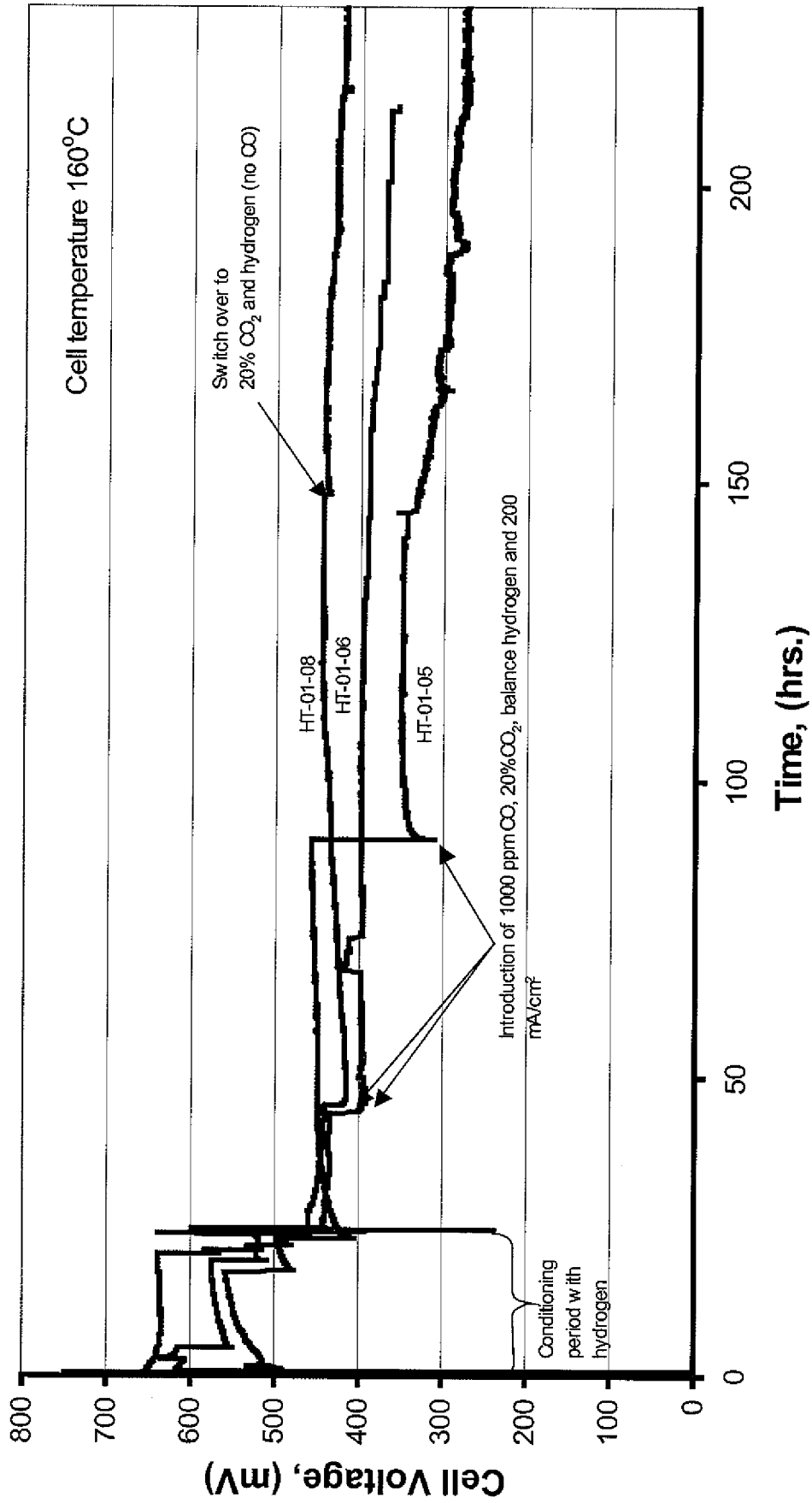
Figure 2. Cell Voltage Improvements with Membrane Optimization Progress

19

As shown on this figure, these three MEAs were operated with a dry anode stream containing 1000 ppm CO, 20% CO_2, and the balance hydrogen. The first MEA and cell tested with this high CO containing stream, designated HT-01-05, showed that the MEA was stable up until the point where the membrane developed a physical leak as was found in the post-test analysis. The small leak allowed crossover that rapidly degraded the cell performance. This MEA operated over 150 hours performing around 350 mV @ 200 mA/cm^2 before it started to falter and was terminated at 250 hours. The next two MEA's fabricated were tested with the same composition anode stream and each performed better than the previous one. The modified MEA, HT-01-06, showed an approximately 50 mV improvement over its predecessor. This MEA operated with steady performance before its endurance started to decay. The third MEA in this figure shows that with additional modifications, HT-01-08, improved more than 100mV over the original MEA adaptation. This MEA eventually operated over 400 hours performing around 410 mV @ 200 mA/cm^2. This MEA started to show decay at 150 hours when it was switched to an alternate stream that did not contain carbon monoxide.

The reason for this decay is not yet well understood. Whatever the reasons for the performance increase and for the decay after about 150 hours, additional diagnostic information is needed. The performance goals are not yet achieved which is targeted as +650 mV at a practical current density of 400 mA/cm^2. A lot of information was gained on the techniques of casting and fabrication as related to MEA quality. Post-test analysis directed modifications for each successive series of MEA fabrication.

As mentioned, all of these first MEA's were first fabricated using the lower viscosity membrane material and it was found that these membranes were not strong enough to operate as a single layer of membrane film, hence two layers were overlapped. This extra layer added contact resistance between the layers to the MEA that decreased its performance. To overcome this unnecessary resistance, a stronger polymer needed to be cast to eliminate the double membrane layers.
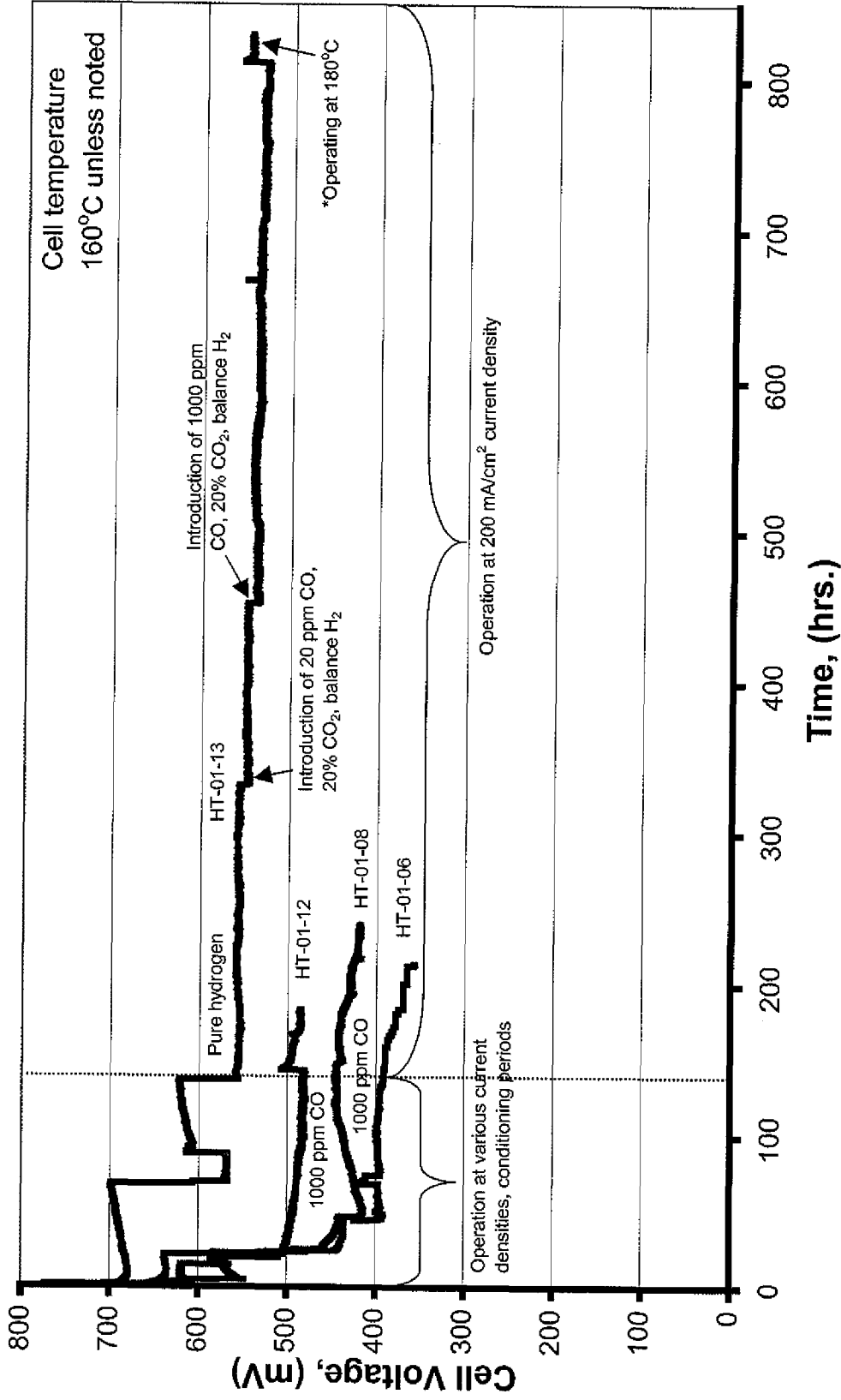
Cell temperature
160°C unless noted

Introduction of 1000 ppm
CO, 20% CO$_2$, balance H$_2$

*Operating at 180°C

Introduction of 20 ppm CO,
20% CO$_2$, balance H$_2$

Pure hydrogen

HT-01-13

HT-01-12

HT-01-08

HT-01-06

1000 ppm CO

1000 ppm CO

Operation at 200 mA/cm^2 current density

Operation at various current
densities, conditioning periods

Cell Voltage, (mV)

800
700
600
500
400
300
200
100
0

Time, (hrs.)

0   100   200   300   400   500   600   700   800

Figure 3. High Temperature MEA Performance Improvements

Acknowledgement